

TRACER DIFFUSION OF SELECTED CATIONS
IN SINGLE CRYSTAL MgO

by

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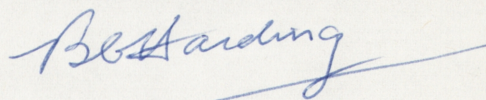
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"The floating of other mens' opinions in our brains
makes us not one jot the more knowing though they happen
to be true."

Locke, Essay, I 4:§23

The work contained in this thesis is my own except where
another source is acknowledged.



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Abstract

The diffusion of various cations in single crystal magnesium oxide has been measured over a wide temperature range using radioactive tracers and a sectioning technique. Self-diffusion studies may be interpreted in such a manner as to suggest that the enthalpy of formation of a Schottky defect in this oxide is (3.8 ± 0.3) eV, while the enthalpy of motion of a cation vacancy is (1.56 ± 0.08) eV.

Intrinsic diffusion occurs above 1900°C , with a 'knee' temperature, for the material used here, of 1800°C . Impurity-precipitation-controlled diffusion has been observed below 1500°C . Atmosphere, apparently, has no effect on diffusion rates. The radius of a diffusing ion seems to have no detectable influence on its enthalpy of motion in MgO , whereas electronic properties (polarisability and charge) are evidently important in this respect. Most impurities diffuse by a vacancy mechanism, but beryllium diffusion may possibly proceed via interstitial sites.

Short-circuit enhancement of diffusion in MgO involves two (or more) mechanisms, one being dependent on the presence of impurity precipitates at dislocations, while the other is independent of this phenomenon and operates for ions which are large compared with the host cation. Such enhancement is believed to have obscured precipitation-controlled lattice diffusion in many studies and also accounts for the variation in activation energies reported by different authors for the diffusion of a given impurity.

1. Introduction

1.1. General remarks

A knowledge of diffusion is basic to an understanding of many phenomena occurring in solids at elevated temperatures. For example, the kinetics of pairing and the growth of nuclei in the process of precipitation both involve diffusion. Under certain conditions, tarnishing is controlled by an outward diffusion of metal ions through an oxide layer. Sintering is a process by which an agglomerate of more or less fine particles bake together upon heating to form a strong, dense body. This has extensive industrial applications and, again, is often diffusion controlled. Other important phenomena involving diffusion include annealing and creep.

Diffusion studies also enable more to be learned about how atoms move in solids and this is related to the study of point defects, their concentrations, formation energies and their movement through the lattice. In conjunction with data obtained from other sources, such as optical and magnetic resonance and electrical conductivity at high and low frequencies, much information can be obtained concerning the defect solid state.

The diffusion characteristics of metals are now well known and a considerable effort has been directed also at the alkali halides, the simplest diatomic compounds. Magnesium oxide forms a bridge between these and more complex materials. Since it has the rock-salt structure and is ionic, one might expect some similarity with the alkali halides, while at the same time, an understanding of the parameters controlling diffusion in MgO could be of value when considering

the more complicated structures encountered, for example, in the field of geophysics.

1.2. Self-diffusion in magnesium oxide

A survey of the literature shows that very few tracer diffusion studies have been carried out in magnesium oxide. The first reported experiments were those of Lindner and Parfitt [1957] in which the self-diffusion of cations was studied using the radio-active isotope Mg-28. This isotope has a short half-life (21.3 h) and therefore it was not possible to cover temperatures below 1400 °C, as this would have entailed unacceptably long annealing times. The single crystals used were claimed to be of very high purity, but an analysis of material [Clarke, 1957] from the same supplier does not bear out this claim. The activation energy of 3.4 eV would seem to be characteristic of intrinsic diffusion, but this interpretation is doubtful when the crystal purity and temperature range are considered. The most recently published experiments include the tracer studies of Harding, Price and Mortlock [1971] and Harding and Price [1972], and the mass spectrometric work of Wuensch, Steele and Vasilos [1972], details of which will be given later.

Anion self-diffusion was measured by Oishi and Kingery [1960] by determining the rate of exchange between a limited volume gas phase, enriched with the stable isotope O-18, and MgO grains. The activation energy obtained was 2.7 eV for the temperature range 1300-1750 °C with an oxide purity of 99.9%. It was concluded that oxygen diffusion was either impurity-controlled or structure sensitive under the conditions of the experiments. O'Keefe [1961] found that the anion self-diffusion coefficient varied approximately as the square root of the oxygen partial pressure. The pressure dependence of D was also investigated by

Rovner [1966] in the temperature range 750-1150 °C using the O-18 isotope exchange method. It was claimed that both intrinsic and extrinsic lattice diffusion were observed and that MgO is an oxygen excess structure with the excess oxygen in interstitial positions.

1.3. Impurity diffusion in magnesium oxide

The tracer diffusion of impurities in magnesium oxide has also received only limited attention. Rungis and Mortlock [1966] measured calcium diffusion in the temperature range 900-1700 °C using an autoradiographic technique, while Harding and Mortlock [1966] have reported data for beryllium diffusion in a similar temperature range. Harding [1967a] later published results for barium diffusion using the tracer Ba-133, and Mortlock and Price [1972] have studied strontium diffusion in MgO. Recently, cadmium diffusion studies have been reported for the temperature range 1800-2300 °C [Harding and Bhalla, 1971] and further data for barium and nickel tracer diffusion have been obtained [Harding, 1972]. Details of these experiments also will be given in this thesis.

The concentration dependence of scandium diffusion in MgO has been reported by Solaga and Mortlock [1970]. Apart from this, and the yttrium diffusion studies of Berard [1971], there has been very little data presented for aliovalent ions in MgO at tracer concentrations.

Other major studies in MgO have been in the field of chemical diffusion, although impurity concentrations have in some cases been fairly low and activation energies have frequently been found to be independent of concentration. Wuensch and Vasilos [1961, 1962, 1965, 1968, 1971] have investigated the diffusion of iron, cobalt, nickel, zinc and calcium in MgO using electron microbeam probe analysis to determine concentration profiles. Similar methods have been used by

Tagai, Iwai, Iseki and Sako [1965] for iron, manganese and chromium, and Blank and Pask [1969] for iron and nickel. Other systems studied have included $\text{MgO-Cr}_2\text{O}_3$ [Greskovich and Stubican, 1970], $\text{MgO-Al}_2\text{O}_3$ [Whitney and Stubican, 1971] and $\text{Mn}_x\text{O-MgO}$ [Jones and Cutler, 1971]. No experiments have been done at temperatures in excess of 1800°C with the exception of the nickel diffusion measurements of Wuensch and Vasilos [1971]. Data appear to relate to extrinsic, impurity-controlled migration in the majority of investigations.

1.4. Short-circuit diffusion in magnesium oxide

Enhancement of diffusion along high-diffusivity paths such as dislocations and grain boundaries has been observed by a number of workers [Zaplatynsky, 1962; Wuensch and Vasilos, 1966; Harding, 1967a; Mortlock and Price, 1972]. It has been concluded that nickel diffusion is only enhanced in the presence of impurity precipitates along grain boundaries [Wuensch and Vasilos, 1966; Mimkes and Wuttig, 1971]. Harding [1971] has suggested that there are two different mechanisms of short-circuit diffusion in MgO and that the important factor in determining which is operating in a given case is cation size. Oxygen grain boundary diffusion has been reported by Rovner [1966] and McKenzie, Searcy, Holt and Condit [1971]. Again the presence of impurities such as iron appears to influence the degree of enhancement measured.

1.5. Electrical conductivity in magnesium oxide

Conductivity and diffusion can be related through the Nernst-Einstein equation in cases where both phenomena depend on the same defect, for example, an effectively charged vacancy. Measurements of the conductivity of MgO have been made by a number of investigators, but it has proved difficult to give a general interpretation of the

results. Mitoff [1959, 1962] concluded that variable valence impurities were responsible for an observed conductivity dependence on oxygen partial pressure. An increasing electronic contribution was found with increasing temperatures. Davies [1963] pointed out that the conductivity data fell into two groups, one agreeing in activation energy with cation self-diffusion (3.5 eV) and the other with oxygen diffusion data (2.7 eV). However, conductivities calculated using the Nernst-Einstein equation from the former agreed much more closely with observations than those calculated from the latter. The dominant current carrier is likely to depend on the oxygen partial pressure surrounding the sample. Lewis and Wright [1968, 1970] favour an anion vacancy mechanism, although conduction by trapped electrons was not ruled out. Alcock and Stavropoulos [1971] conclude that conductivity in the range 900-1180 °C is cationic. Finally, Osburn and Vest [1971] proposed that at high oxygen pressures the dominant defects are holes and singly ionised magnesium vacancies, while at low oxygen pressures, electrons and doubly ionised oxygen vacancies dominate. In contrast to Mitoff's results, it was found that the pressure dependence of the conductivity decreased with increasing impurity concentrations. These data were obtained in the temperature range 1000-1600 °C.

1.6. Aim of the present study

Many of the diffusion studies with MgO have been in the extrinsic region and have involved chemical diffusion. Furthermore, it is evident that conductivity measurements are of little use in clarifying diffusion problems in this material. The work presented here includes the measurement, by tracer techniques, of cation self-diffusion and the diffusion of selected impurities over the temperature range 1000-2500 °C in single crystal magnesium oxide, the aim being to

determine the parameters controlling diffusion and to evaluate defect formation and migration energies.

2. The Basic Theory of Diffusion

2.1. Fick's laws and solutions to the diffusion equation

If there exists a concentration gradient of solute, A, in a solvent, B, then there will be a flux, J, of A atoms crossing unit area per second given by

$$J = -D \text{ grad } c \quad (2.1)$$

where c is the concentration of A atoms in the plane considered and D is the diffusion coefficient. This is Fick's first law. Applying the continuity condition

$$-\frac{\partial c}{\partial t} = \text{div } J \quad (2.2)$$

we can obtain from equation (2.1) Fick's second law of diffusion, namely

$$\frac{\partial c}{\partial t} = \text{div}(D \text{ grad } c) . \quad (2.3)$$

Assuming D to be independent of concentration (and hence of position) and restricting the problem to one dimension we obtain

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} . \quad (2.4)$$

In experiments to be described here, a trace quantity, M , of solute is deposited on one end of what can be regarded as a long bar of solute-free material. This system is annealed at a controlled temperature for a time, t , so that diffusion occurs. There are two sets of boundary conditions of interest here. If the deposited layer dissolves in the host lattice in a time very much less than t , the amount of diffusing material remains constant throughout the experiment. The solution to

equation (2.4) under these conditions is

$$c = \frac{M}{\sqrt{\pi Dt}} \exp(-x^2/4Dt) \quad (2.5)$$

satisfying the requirements that

$$x > 0 \quad \text{for} \quad c \rightarrow 0 \quad \text{as} \quad t \rightarrow 0$$

$$x = 0 \quad \text{for} \quad c \rightarrow \infty \quad \text{as} \quad t \rightarrow 0$$

and

$$\int_0^{\infty} c(x,t) dx = M.$$

The second possibility is that the deposited solute never completely dissolves and as material diffuses away from the interface it is replaced by more of the deposit going into solution. The effective surface concentration remains constant at the saturation level. In this case, the solution to (2.4) is given by

$$c = c_s \operatorname{erfc} x/2\sqrt{Dt} \quad (2.6)$$

provided the deposited solute layer is of negligible thickness. This satisfies the requirement that

$$c = 0 \quad \text{at} \quad t = 0 \quad \text{for} \quad 0 < x < \infty$$

$$c = c_s \quad \text{at} \quad x = 0 \quad \text{for} \quad 0 < t < \infty.$$

The total amount of material in solution at a time, t , is

$$M_t = \int_0^{\infty} c_s \operatorname{erfc} x/2\sqrt{Dt} dx$$

whence

$$M_t = 2c_s \sqrt{\frac{Dt}{\pi}}. \quad (2.7)$$

2.2. The temperature dependence of the diffusion coefficient

From experimental data obtained at different temperatures, the temperature dependence of D can be determined. In general, it is found that a graph of $\log D$ vs. $1/T$ is linear, indicating that one can write an Arrhenius type equation, i.e.

$$D = D_0 \exp(-\epsilon/kT) \quad (2.8)$$

where ϵ is the experimental activation energy, D_0 is the 'pre-exponential' or 'frequency' factor and k is Boltzmann's constant.

2.3. Relationships between experimental diffusion coefficients

It should be noted briefly that equation (2.1) can be used to define a 'diffusion coefficient' regardless of what forces or gradients are present. This leads to various kinds of diffusion coefficients. If two semi-infinite bars of differing proportions of components A and B are joined together and diffused, the Boltzmann-Matano solution (see, for example, Shewmon [1963], p.28) leads to one coefficient, $\tilde{D}$, which completely describes the resulting homogenisation. $\tilde{D}$ is often called the interdiffusion coefficient. Darken [1948] has published an analysis relating $\tilde{D}$, at a given composition, to the self-diffusion coefficients, D_A and D_B , for each component, at the same composition. The result is

$$\tilde{D} = D_A n_B + D_B n_A \quad (2.9)$$

where n_A and n_B are the appropriate mole fractions of each component. D_A can be related to the tracer diffusion coefficient, D_A^* , as follows [Shewmon, 1963, p.125]

$$D_A = D_A^* \left(1 + \frac{d \ln \gamma_A}{d \ln n_A} \right) \quad (2.10)$$

where γ_A is the activity coefficient of component A. A similar equation can be written for B. It can be seen that the diffusion coefficient for A in a chemical concentration gradient, D_A , is not equal to the value, D_A^* , obtained in a self-diffusion tracer experiment, except for ideal or dilute solutions. It can be shown from thermodynamics that

$$n_A \frac{d \ln \gamma_A}{d \ln n_A} = n_B \frac{d \ln \gamma_B}{d \ln n_B} \quad (2.11)$$

Using this relation and equations (2.9) and (2.10) we arrive at the following expression

$$\tilde{D} = \left(D_{AB}^* + D_B^* n_A \right) \left(1 + \frac{d \ln \gamma_A}{d \ln n_A} \right) \quad (2.12)$$

which links the three most commonly measured diffusion coefficients $\tilde{D}$, D_A^* and D_B^* . In the work presented here, we shall usually refer only to tracer diffusion coefficients and hence the asterisk will be dropped.

2.4. Random walk treatment of diffusion

It can be shown from random walk theory that the mean square displacement, $\langle X^2 \rangle$, of an atom performing a series of n elementary jumps to z possible nearest neighbour lattice sites is given by

$$\langle X^2 \rangle = \left\langle \sum_{j=1}^z n_j x_j^2 \right\rangle \quad (2.13)$$

where n_j is the number of jumps in the direction of the j^{th} nearest neighbour and x_j is the x displacement of such a jump. If we define a frequency, Γ_j , by the equation

$$\Gamma_j = \langle n_j \rangle / \tau \quad (2.14)$$

we obtain

$$\langle X^2 \rangle = \tau \sum_{j=1}^Z \Gamma_j x_j^2 \quad (2.15)$$

where τ is the time interval over which the series of displacements occurs. For a random walk in the absence of driving forces, the diffusion coefficient is given by

$$D = \frac{\langle X^2 \rangle}{2\tau} \quad (2.16)$$

(see for example Manning [1968]). From equations (2.15) and (2.16) we therefore obtain the important equation

$$D = \frac{1}{2} \sum_{j=1}^Z \Gamma_j x_j^2. \quad (2.17)$$

In the case of a simple cubic structure, for example, this relation gives

$$D = \frac{1}{6} \lambda^2 \Gamma \quad (2.18)$$

where λ is the jump distance and Γ the jump frequency.

2.5. Calculation of the jump frequency, Γ

There are two approaches to this problem, the equilibrium method based on the theory of rate processes [Glasstone, Laidler and Eyring, 1941] and the dynamical theory of Rice [1958].

In the equilibrium approach, it is assumed that the diffusing species jumps from one position to the next after surmounting a critical energy barrier, and that having attained this activation energy, it continues to the final equilibrium state. The jumps are treated as transitions between energy states that are sufficiently long lived to come into thermal equilibrium with the lattice. If the 'activated complex' occupies a region of length δ at the top of the energy barrier, its mean life-time will be $\delta/\bar{v}_x$, where $\bar{v}_x$ is the mean

velocity of the complexes as they cross the barrier in the x direction. The jump frequency (equivalent to the probability of an atom crossing the barrier) is

$$\Gamma = \frac{n^\ddagger}{n_1} \frac{\bar{v}_x}{\delta} = \frac{n_3}{n_1} \bar{v}_x \quad (2.19)$$

where $n^\ddagger$ and n_1 are the number of atoms in the activated and stable states respectively and $n_3 = n^\ddagger/\delta$. The mean velocity, $\bar{v}_x$, can be calculated from the Maxwell-Boltzmann law and the ratio n_3/n_1 is equal to the ratio of the partition functions for atoms in the activated and stable states. Upon evaluation, it is found that

$$\Gamma = v \exp(-\Delta g_m/kT) \quad (2.20)$$

where Δg_m is the free energy of migration and v is an effective vibrational frequency for an atom in an equilibrium position.

The equation for D now becomes, from equation (2.17),

$$D = \gamma \lambda^2 v \exp(-\Delta g_m/kT) \quad (2.21)$$

where γ is a numerical factor determined by the correlation factor (accounting for non-random jumps), the number of nearest neighbour sites and by a statistical factor accounting for the occurrence of backward or forward motion, and λ is the jump distance. Since

$$\Delta g_m = \Delta h_m - T\Delta s_m \quad (2.22)$$

we can write

$$D = \gamma \lambda^2 v \exp(\Delta s_m/k) \exp(-\Delta h_m/kT) \quad (2.23)$$

and comparison with equation (2.8) shows that

$$D_o = \gamma \lambda^2 v \exp(\Delta s_m/k) . \quad (2.24)$$

Vineyard [1957] has given the most general and rigorous treatment of the equilibrium approach, in which the jump rate, Γ , is displayed as a product of an effective frequency, ν^* , and an activation exponential, with the activation energy being the difference in potential between the equilibrium site and the top of the barrier. The effective frequency is given by

$$\nu^* = \frac{\prod_{j=1}^N \nu_j}{\prod_{j=1}^{N-1} \nu'_j} \quad (2.25)$$

where the ν_j 's are the N normal frequencies of the entire system in the ground state and the ν'_j 's are the $N-1$ normal frequencies in the excited state.

In the dynamical theory, Rice [1958] has developed a formalism based on the actual vibrational modes of the atoms. Before an atom can change sites, it has to move to the saddle point at the same time that the restraining atoms move out of the way. It is assumed that the movement of a particular atom will be that which results from the superposition of the displacements due to the elastic waves in the region of the atom concerned. If the various waves occur with random phases, they will occasionally superimpose to give the displacements required for a jump. Using this analysis, an equation of the same form as (2.20) is obtained, but in this case the quantities which replace ν and ΔG_m are expressed in terms that can be explicitly summed. This procedure avoids the requirement that the activated complex be in thermal equilibrium with the lattice, but to simplify the mathematics involved, it is assumed that the forces between atoms are harmonic. For the large displacements involved, this is not a good approximation. Manley [1960] has demonstrated that the activation energy may be calculated directly from the atomic force constants without resorting to normal mode analysis. However, there has been little practical application of these results.

3. Diffusion in Ionic Solids - Theory

3.1. Mechanisms of diffusion and lattice defects

In the derivation of equations (2.17) and (2.18), nothing was said concerning mechanisms of diffusion or the availability of sites into which the diffusing atom or ion could move. The jump process alone was considered. If the probability of a suitable neighbouring site being vacant is p_v , then we can write

$$D = \gamma \lambda^2 \Gamma p_v . \quad (3.1)$$

For an interstitial solute in a very dilute binary alloy, Γ is independent of composition and p_v is essentially unity. In general, p_v is equal to the fraction of sites vacant, n , and the calculation of this fraction depends on the diffusion mechanism concerned. Several possible mechanisms have been postulated (see, for example, Shewmon [1963]; Manning [1968]). The principal ones occurring experimentally are the vacancy, interstitial and interstitialcy mechanisms, the latter involving both lattice and interstitial sites. In an ionic solid, atomic defects fall into two categories, those which are inherent in the thermodynamics of the solid state and those which are specific to the sample considered. Inherent defects are of two types. In the simple case of a stoichiometric compound MX, a Schottky defect consists of a vacant cation lattice site and a vacant anion lattice site. A Frenkel defect consists of an interstitial ion and a corresponding vacant lattice site. In order to obtain a complete expression for D , it is necessary to obtain equations for the concentration of these defects.

3.1.1. Equilibrium concentration of Schottky defects

To calculate the number of Schottky defects in thermodynamic equilibrium at a given temperature, an explicit expression for the free energy of the crystal, ΔG , in terms of the number of defects must be obtained. ΔG is then minimised with respect to the number of defects, n_s , present at equilibrium. The configurational entropy term in ΔG is evaluated statistically using Stirling's approximation. If $2N$ is the total number of anion and cation sites and g_s is the energy required to form one cation vacancy and one anion vacancy, it can be shown that

$$n_s = N \exp(-g_s/kT) \quad (3.2)$$

where $n_s \ll N$ (i.e. when there are relatively few defects).

3.1.2. Equilibrium concentration of Frenkel defects

The number of Frenkel defects in a crystal is calculated in a similar manner to that used for Schottky defects. It can be shown that

$$n_f = \sqrt{NN'} \exp(-g_f/kT) \quad (3.3)$$

where n_f is the number of vacant sites (and the number of associated interstitials), g_f is the energy to form one defect, N is the number of lattice sites and N' is the number of interstitial sites.

3.1.3. Equations for the diffusion coefficient

We can now write complete expressions for the diffusion coefficient in ionic crystals for the case where intrinsic (thermally produced) defects are dominant. For diffusion by a vacancy mechanism, we obtain from equations (2.20), (3.1) and (3.2)

$$D = \gamma \lambda^2 \nu \exp(-\Delta g_m/kT) \exp(-g_s/kT) . \quad (3.4)$$

Using equation (2.22), this may be written as

$$D = \gamma \lambda^2 v \exp[(\Delta s_m + s_s/2)/k] \exp[-(\Delta h_m + h_s/2)/kT] . \quad (3.5)$$

Comparison with the Arrhenius equation (2.8) shows that the activation energy (ϵ) in this case is equal to $\Delta h_m + h_s/2$ and the pre-exponential factor is

$$D_o = \gamma \lambda^2 v \exp[(\Delta s_m + s_s/2)/k] . \quad (3.6)$$

Similar expressions can be obtained for D in crystals where Frenkel defects are dominant using equations (2.20), (3.1) and (3.3).

3.2. Factors influencing defect concentrations

3.2.1. Vacancy pairing

In ionic crystals of the type MX , the intrinsic defects are commonly of the Schottky type and the mass action equation governing their concentration is

$$n_c n_a = n_o^2 = k_s \quad (3.7)$$

where n_c and n_a are the mole fractions of cation and anion vacancies respectively. In a pure compound these are both equal to n_o . The equilibrium constant k_s is given by

$$k_s = \exp(-g_s/kT) . \quad (3.8)$$

In thermal equilibrium, these relations always apply whether the Schottky defects are dominant or not. However, interactions between defects are neglected in equation (3.7) and in ionic solids, effective charges associated with these defects give rise to coulombic interactions. This interaction can be taken into account using the Debye-Hückel theory of electrolytes [Lidiard, 1957] and attempts have been

made to obtain an accurate description by Allnatt [1967].

Defect interactions are not accurately coulombic when they are close together and it is better to describe close pairs as distinct defects. The mole fraction of vacancy pairs is given by

$$n_p = z \exp(-g_p/kT) \quad (3.9)$$

where z is the number of distinct orientations of the pair (= 6 for an NaCl type lattice), and g_p is the free energy of formation of the pair. It should be noted that the concentration of pairs formed in this way is independent of the separate concentrations of single cation and anion vacancies (see for example, Lidiard and Tharmalingam [1959]). Furthermore, although they may be important in diffusion, having no net charge, they do not contribute to the low frequency electrical conductivity.

3.2.2. The effect of impurities

Consider now a crystal containing a mole fraction c_i of aliovalent impurity ions. The simplest situation and one most frequently studied, is that of c_i divalent cations in an alkali halide. Because of the need for electrical neutrality, each substituted divalent ion yields one cation vacancy, and the condition for neutrality is

$$n_c = c_i + n_a. \quad (3.10)$$

From equation (3.7) the concentration of cation vacancies is now given by

$$n_c = \frac{c_i}{2} \left[1 + \left(1 + 4n_o^2/c_i^2 \right)^{\frac{1}{2}} \right]. \quad (3.11)$$

The concentration of anion vacancies is given by

$$n_a = \frac{c_i}{2} \left[\left(1 + 4n_o^2/c_i^2 \right)^{\frac{1}{2}} - 1 \right] \quad (3.12)$$

and is strongly suppressed by the presence of the impurity.

When $n_o \ll c_i$, the concentration of defects is controlled by the impurity concentration alone and is essentially constant. In this 'extrinsic' temperature range, D is given by

$$D = \gamma \lambda^2 v n_c \exp(-\Delta g_m/kT) \quad (3.13)$$

and the activation energy, ϵ , is equal to the enthalpy of cation motion, Δh_m . In the case of a divalent impurity in NaCl, n_c is equal to c_i in equation (3.13), but for a trivalent ion in MgO, n_c is equal to $c_i/2$.

3.2.3. Impurity-vacancy association

Because of the effective charges on an aliovalent ion and a cation vacancy, there exists a coulombic attraction between them. From the law of mass action, the equation for the concentration, n_k , of these stable pairs is

$$n_k [n_c (c_i - n_k)]^{-1} = z \exp(g_k/kT) \quad (3.14)$$

where z is the number of distinct orientations of the pair (= 6 in MgO for a tetrahedral complex or 12 for an orthorhombic complex). The condition for electrical neutrality is now

$$n_c = n_a + n_i - n_k \quad (3.15)$$

where n_i is the number of vacancies arising from an aliovalent impurity (= c_i for divalent ions in a monovalent lattice and $c_i/2$ for trivalent ions in a divalent lattice). As before, long-range effects can be accounted for by the Debye-Hückel theory. Higher complexes of

impurities and vacancies may also occur and are important at low temperatures and high impurity concentrations, especially in the precipitation of impurities out of solution (e.g. Cook and Dryden [1962]). A further point that should be made is that isolated ions cannot diffuse by a vacancy mechanism unless a 'complex' is formed. Indeed, vacancy diffusion can be approached from this point of view, the critical factor being the lifetime of the complex.

3.2.4. Impurity solubility

Under appropriate conditions of temperature and concentration, it is possible that some of the impurity present in a given crystal will precipitate to form aggregates of a separate phase. This will affect the compensating vacancy concentration and hence D . The mass action equation for the concentration of free impurity ions in solution, c'_i , is

$$c'_i n_c = c'_i (c'_i + n_a) = \exp(-g_d/kT) \quad (3.16)$$

where g_d is the free energy of solution. When $n_a \ll c'_i$ as is usual, we have

$$c'_i = \exp(-g_d/2kT) . \quad (3.17)$$

Equations (3.16) and (3.17) apply for the case of a divalent impurity in a monovalent host lattice, e.g. MgCl_2 in KCl [Lidiard, 1957]. In this case, the activation energy for diffusion in the impurity-precipitation range is $\Delta h_m + h_d/2$ where h_d is the enthalpy of solution.

3.2.5. Non-stoichiometry

There are three ways by which a stoichiometric imbalance can occur in a crystalline compound, MX . Substitution of some atoms of one

component into the sublattice of the other is sometimes possible, usually in the case of an alloy. Additional M or X can be incorporated interstitially, this being analogous to Frenkel defects except that the numbers of interstitials and vacant lattice sites are no longer equal. The third way in which non-stoichiometry can arise is analogous to the Schottky form of disorder, with the numbers of M and X vacancies being no longer equal. For a crystal in contact with its vapour, it is possible to write equations for the creation and annihilation of vacancies such as



where following Kröger [1964], M_M^X represents an effectively neutral M ion on a site in the M sublattice, $M(g)$ is an M atom in the vapour phase and V_M^X is an effectively neutral M vacancy. A similar notation is applicable to the X component. Vacancies are often more stable in the ionised state with respect to the lattice, such ionisations being represented as



where V_M' is an M vacancy with a single effective negative charge and $h \cdot$ is a positive hole. Each of these reactions has associated with it a 'heat of reaction'. Naturally, because they involve vacancy concentrations, reactions such as (3.18) and (3.19) can influence diffusion. However, if anions and cations evaporate in equal numbers, as is likely in MgO (see later), stoichiometry is maintained. On the other hand, reactions such as



are encouraged by the presence of variable valence impurities even in stoichiometric compounds, but they need not be the dominant reaction involving vacancies. Evidence for this type of reaction in MgO will be discussed later.

It was mentioned in the Introduction that O'Keeffe [1961] and Rovner [1966] had both found a pressure dependence of the anion diffusion coefficient in MgO which suggests the presence of oxygen interstitials under certain conditions. The reactions concerned in this case are



where O_i^x , O_i' and O_i'' are oxygens on interstitial sites. However, since reaction (3.22) is the most likely, the cation vacancy concentration is very little affected, if at all, and this will not be discussed further.

3.3. Diffusion and ionic conductivity

Diffusion may occur with both neutral and charged imperfections whereas conduction can only occur through charged defects. If diffusion and conduction involve the same defect, the following equation holds

$$\frac{\sigma}{D_T} = \frac{c q_v^2}{f k T} \quad (3.25)$$

where D_T is the tracer diffusion coefficient, σ is the conductivity, q_v is the effective charge on the defect (a vacancy in this case), c is the number of ion sites per unit volume and f is the correlation factor. By means of this equation (the Nernst-Einstein equation) it is possible

to gain some insight into the mechanisms of conduction and diffusion operating in a given material. However, its application to data for MgO has not been of much value. Diffusion coefficients calculated by means of equation (3.25) from conductivity data agree quite well with the published diffusion data, but it is apparent that conduction is not entirely ionic - in fact, under certain conditions the ionic transport number is very small. For this, and other reasons discussed later, no use will be made of equation (3.25) in this work except to note that if holes and vacancies are produced by reactions like (3.21), the oxygen partial pressure dependence found for conduction, should also apply to diffusion.

4. The Measurement of Tracer Diffusion in MgO

4.1. Radioactive tracer and sectioning techniques

The use of radio-isotopes is a convenient means of studying diffusion at near-zero concentrations. No significant error is introduced if the diffusion coefficient for a particular isotope is taken as being applicable to all isotopes of the same element. There are a number of methods that can be used to determine diffusion profiles. The sectioning method involves the depositing, by some means, of the tracer on a plane end face of what can be regarded as a semi-infinite piece of material. After diffusion, successive thin slices of material, the planes of which are parallel to the plane of the original tracer deposit and perpendicular to the diffusion direction, are removed and their activity measured. In this way, a profile of concentration versus penetration can be plotted. In this work, however, it was found more convenient to measure the activity remaining in the bulk of the crystal, because not only were the slices removed very thin (sometimes less than 1 μm), but the specific activities in several experiments were very low. This procedure leads to integrated diffusion profiles. At any depth, x' , from the original surface, the activity remaining is given by

$$A(x') = \int_{x'}^{\infty} c(x) dx . \quad (4.1)$$

This is valid for a given annealing time, t , when the constant of proportionality between count rate and concentration has been omitted.

At $x' = 0$ we have

$$A(0) = \int_0^{\infty} c(x) dx . \quad (4.2)$$

It is convenient to consider a 'fractional activity remaining' $F(x')$ given by

$$F(x') = \frac{\int_{x'}^{\infty} c(x) dx}{\int_0^{\infty} c(x) dx} \quad (4.3)$$

The concentration function is given by either equation (2.5) or equation (2.6), depending on the solubility of the tracer material in the host lattice (see section 2.1.). Substituting equation (2.5) into (4.3) gives

$$F(x') = \frac{\int_{x'}^{\infty} \exp(-x^2/4Dt) dx}{\int_0^{\infty} \exp(-x^2/4Dt) dx} \quad (4.4)$$

whence it can be shown [de Bruin and Watson, 1964; Harding, 1967a] that

$$F(x) = \text{erfc}(x/2\sqrt{Dt}) \quad (4.5)$$

where 'erfc' is the error function complement and the primes have been dropped. Therefore, plotting $\text{erfc}^{-1} F(x)$ against penetration distance, x , gives a straight line of slope $1/2\sqrt{Dt}$ from which D is obtained.

Similarly, insertion of (2.6) into (4.3) yields

$$F(x') = \frac{\int_{x'}^{\infty} \text{erfc}(x/2\sqrt{Dt}) dx}{\int_0^{\infty} \text{erfc}(x/2\sqrt{Dt}) dx} \quad (4.6)$$

It should be pointed out that in this case, the denominator ($\equiv A(0)$) is not the initial activity recorded from the crystal before sectioning begins, but the point where the extrapolated experimental plot of $A(x)$ vs. x cuts the $x = 0$ axis. It represents the count rate from the total amount of material in solid solution after annealing of the crystal. The denominator on the right of equation (4.6) is again a standard integral and it can be shown that

$$F(x) = 1.772 \operatorname{ierfc}(x/2\sqrt{Dt}) \quad (4.7)$$

where 'ierfc' is the integrated error function complement. A graph of $\operatorname{ierfc}^{-1} F(x)/1.772$ vs. x gives a straight line of slope $1/2\sqrt{Dt}$ and D can be found.

So far it has been assumed that the absorption of radiation in MgO is negligible. This is indeed so for many isotopes over the penetration distances involved. Where absorption is significant, the Gruzin [1952] method can be used to obtain D . The contribution to the activity remaining from a slice of thickness dx after material has been removed to a distance x_n from the original surface is given by

$$dA = Kc(x) \exp[-\mu(x - x_n)] dx \quad (4.8)$$

where K is a constant relating activity to concentration, μ is the absorption coefficient for the radiation concerned and absorption is assumed to be exponential. The total activity remaining is then given by

$$A_n = K \int_{x_n}^{\infty} c(x) \exp[-\mu(x - x_n)] dx \quad (4.9)$$

Evaluation of the integral (see for example, Adda and Philibert [1966]) leads to the equation

$$A_n - \frac{1}{\mu} \frac{\partial A_n}{\partial x_n} = \left(\frac{K}{\mu} \right) c(x_n) \quad (4.10)$$

We can write a normalised corrected activity at a penetration distance x as

$$f(x) = \left[\frac{A(x) - \frac{1}{\mu} \frac{\partial A(x)}{\partial x}}{A(o) - \frac{1}{\mu} \frac{\partial A(o)}{\partial x}} \right] \quad (4.11)$$

If $c(x)$ is given by equation (2.5) then (4.10) becomes

$$f(x) = \exp(-x^2/4Dt) \quad (4.12)$$

and a graph of $\log f(x)$ against x^2 gives a line of slope $-1/4Dt$ and hence D is obtained. Similarly, substituting equation (2.6) into (4.10) leads to

$$f(x) = \operatorname{erfc}(x/2\sqrt{Dt}) \quad (4.13)$$

and plotting $\operatorname{erfc}^{-1} f(x)$ against x will enable D to be calculated.

For most of the tracers used in this work (see section 4.2.2.) μ is small and μA_n can be neglected in comparison with $\partial A_n / \partial x_n$. Equations (4.5) and (4.7) satisfactorily describe the experimental data. Equation (4.10) was used for Ni-63 and Ca-45, although the second term on the left hand side is small for nickel ($\mu \sim 5000 \text{ cm}^{-1}$) and an error of only about 5% is introduced into D if it is neglected altogether.

4.2. Materials and apparatus

4.2.1. Magnesium oxide single crystals

Magnesium oxide has the rock-salt structure, that is, it consists of two face-centred cubic sublattices. The lattice parameter is $4.2 \text{ \AA}$, so that the shortest jump distance between two sites in either sublattice is $2.95 \text{ \AA}$. The single crystals cleave most easily in the $[100]$ planes.

The material used in this work was obtained from two sources. A few crystals were supplied by the Monocrystals Co., Cleveland, Ohio, in the form of right cylinders $\frac{1}{4}$ " in diameter and $\frac{1}{4}$ " long, the end faces being $[100]$ planes. The bulk of the MgO was supplied by Ventron Electronics, Bradford, Pennsylvania, as rectangular blocks several centimetres long by 1 cm cross section, the faces again being $[100]$ cleavage planes. Both suppliers claimed 99.99% nominal purity. However, in view of the importance of impurities in diffusion processes, samples of both types of crystal were analysed by the Chemistry Division of the

Australian Atomic Energy Commission. Table 4.1 shows the results of this analysis (in mole ppm) together with data for material from other suppliers [see Wuensch et al., 1972]. It can be seen that there was very little difference between the Ventron and Monocrystals samples and that the major aliovalent impurity present was iron. Electron spin

Table 4.1. Analysis of MgO single crystals from various sources, giving impurities present in mole ppm (divalent elements excluded)

Impurity element	Mole fraction (ppm)			
	V	M	N	S
Na	15	20	30	30
Al	20	30	30	20
Si	3	11	50	5
S			15	8
Cl			7	14
K	4	4	7	7
Cr	6	8	4	2
Mn	4	5	9	1
Fe	85	85	128	21
Zr			3	
Estimated cation vac. concn.	60	60	120	10

V - Ventron Electronics Corp.
M - Monocrystals Co.
N - Norton Co.
S - W. and C. Spicer Ltd.

resonance measurements (by Dr. R. Bramley of the Research School of Chemistry, ANU) confirmed the presence of 85 ppm iron with the Fe^{3+} : Fe^{2+} ratio equal to approximately 10:1. These measurements also indicated 15 ppm Mn^{4+} in the Ventron material rather than the 4 ppm quoted in Table 4.1.

Dislocation densities in the Monocrystals MgO have been discussed in earlier work [Harding, 1967a] and appear to be somewhat high ($\sim 10^7$ per cm^2) probably because of the obvious use of core-drilling to produce the cylindrical samples. The extent of such damage in the Ventron material is unknown, but it could have been smaller as the samples had been cleanly cleaved from the bulk, rather than drilled. The influence of dislocations on diffusion in MgO will be discussed later.

4.2.2. The precision grinder

A grinder of the simplest design gave good results and penetration distances of 10-20 μm could be handled easily. In some cases, where annealing was carried out at relatively low temperatures, $\sqrt{Dt}$ was only about 1-2 μm . The grinder is shown in figure 4.1. It consisted of an accurately machined cylinder and a close fitting piston. The latter was held in place by a guide pin running in a groove along its length. The cylinder was about 6.5 cm in diameter and its end faces and those of the piston were parallel to within 5 μm over this distance. The sample to be sectioned was attached to one end face of the piston with metallurgical mounting plastic (North Hill Plastics, London) which was soluble in chloroform. Sections were removed by working the grinder assembly against plate glass using 1 μ diamond paste as an abrasive. The section thickness was measured using a dial gauge and was usually in the range 0.5-3.0 μm depending on the total penetration expected. For a crystal side of about 0.4 cm, the diffusion face could be set parallel to the glass with an accuracy of better than 0.05%. In other words, sections removed were perpendicular to the diffusion direction to this accuracy. In a number of cases, the diffusion face was no longer accurately flat after annealing and this led to misalignment

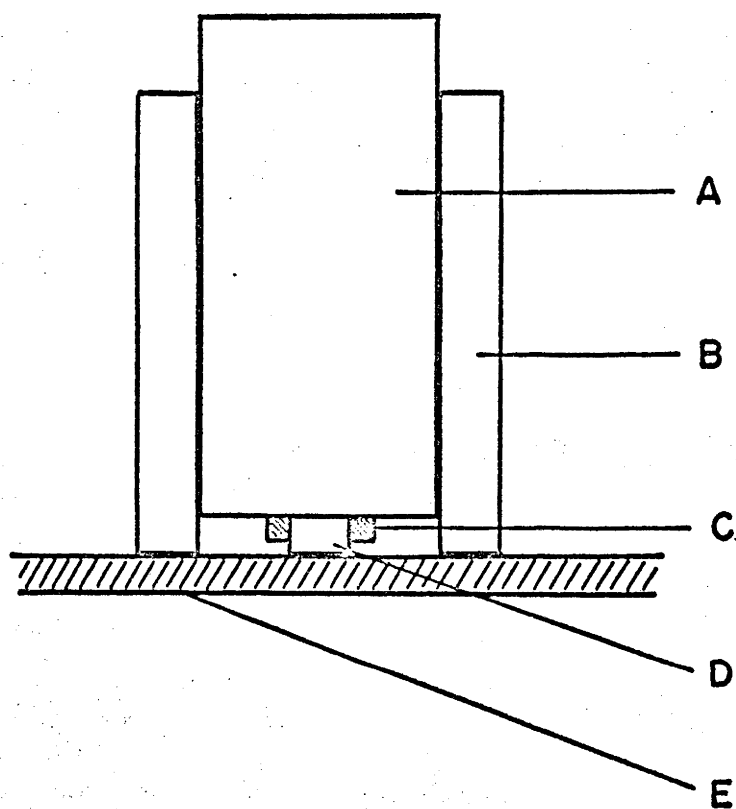


Figure 4.1. A diagrammatic representation of the steel precision grinder used for sectioning diffused MgO samples.

A - piston; B - cylinder; C - mounting plastic; D - MgO crystal;
E - glass plate.

when the sample was mounted on the grinder piston. Misalignments greater than 2μ were not accepted because these involved distances that could approach $\sqrt{Dt}$.

4.2.3. Radioactive tracers and detection equipment

If an isotope is to be useful in diffusion work, its half-life should be sufficiently long, it should be available in high specific activity and it must have a characteristic radiation that can be separated from that of any active daughters produced. In some cases, the radiation from the daughter can be used. Table 4.2 lists details of the tracers used in this study.

Table 4.2. Details of the radioactive tracers used in the diffusion studies reported in this thesis

Tracer	Radiation counted	$t_{1/2}$	Total activity	Specific activity	Supplier
Mg-28	γ	21.3 h	0.12 mCi	4 mCi/g	AAEC
Be-7	γ	53 d	1 mCi	C.F.	RCC
Ba-133	γ	10 y		10 Ci/g	NEN
Ca-45	β	164 d	1 mCi	8 Ci/g	RCC
Cd-115m	β	43 d	1 mCi	0.3 Ci/g	RCC
Ge-68	annih ⁿ . γ	270 d	0.5 mCi	C.F.	NEN
Ni-63	β	125 y	20 mCi	5 Ci/g	ORNL

C.F. - Carrier free
 AAEC - Australian Atomic Energy Commission
 RCC - Radiochemical Centre, Amersham
 NEN - New England Nuclear, Boston, Mass.
 ORNL - Oak Ridge National Laboratory, Tennessee

It will be noted that the only tracer available for measurements of cation self-diffusion in MgO is Mg-28 with a half-life of 21.3 hours. Fortunately, this tracer was obtainable from the Isotope Division of the Australian Atomic Energy Commission and could therefore

be in use in this laboratory only a few hours after production.

Precision grinding methods minimised annealing times, but even so, many batches of tracer were required to obtain sufficient data over a wide temperature range. The details given for Mg-28 in Table 4.2 refer to a typical delivery.

A single channel gamma spectrometer was used for the detection of tracers emitting gamma rays and a Geiger-Müller end window counter for the counting of beta-radiation. These systems were assembled from interchangeable modules manufactured by Canberra Industries ('1400' series) and ORTEC ('400' series) according to the United States Atomic Energy Commission's N.I.M. specifications. The scintillation detector included a 2" × 2" thallium-activated sodium iodide crystal while the G-M tube was halogen quenched and operated at a convenient 550 V. Samples were shielded from background radiation with a commercial lead castle manufactured by ECKO and modified to accept the detector and grinder piston with the MgO crystal attached. A selection of standard sources was available with which to calibrate the spectrometer, including Ba-133, Be-7, Cs-137 and Co-60. Counting was done in an air-conditioned room and once the equipment was calibrated, it proved unnecessary to make any further adjustment during a given experiment. A standard was used, however, to check that no drifting occurred and to correct for radioactive decay in the case of relatively short-lived tracers.

4.2.4. Furnaces and temperature measurement

For pre-annealings and the occasional diffusion-annealing at temperatures up to 1250 °C, a 'Kanthal' wound electrical resistance furnace manufactured by A.D.A.M.E.L. (Paris) was used. The temperature in the hot zone of this furnace could be controlled to within one

degree by the expansion and contraction of a rod set into the former on which the element was wound. For temperatures up to 1750 °C, two Johnson-Matthey platinum-rhodium wound resistance furnaces (type TK2) were used. One was controlled by a Cambridge two-step indicator-controller using a Pt-Pt/10% Rh thermocouple as sensor, the other by a Leeds and Northrup 'Rayotube' total radiation pyrometer coupled to a Leeds and Northrup 'H' type controller-recorder.

Temperatures up to 1500 °C were measured independently of the furnace control units using a Leeds and Northrup potentiometer (type K-3) and Pt-Pt/10% Rh thermocouples. For readings up to 1750 °C, a Pt/5% Rh - Pt/20% Rh thermocouple was employed. A continuous record was also kept with a multichannel recorder (Leeds and Northrup, type W). Sunvic CJ1 electric cold junctions were used to eliminate the effects of ambient temperature variations. All thermocouples and the potentiometer were calibrated initially by the National Standards Laboratory, Sydney. (Subsequently, some thermocouples were calibrated at the gold point in this laboratory.) The accuracies quoted were generally 0.2% for the thermocouples and 0.1% for the potentiometer readings. (This, of course, was not the accuracy to which the temperature for a complete diffusion run could be measured.)

For diffusion annealings up to 2500 °C, a furnace made by Spemby Technical Products, Ltd. (Kent, England) was used, with minor modifications. A diagram of the furnace assembly is shown in figure 4.2. It consisted of two parts, a water-cooled, stainless steel base and a graphite insulated hood. Water-cooled electrodes passed through the base and supported a tubular, slotted graphite element mounted in a vertical position. This element was clamped in position with an insulating ceramic cone. The hood consisted of a vacuum vessel with a water-cooled outer jacket and an inner graphite lining containing graphite

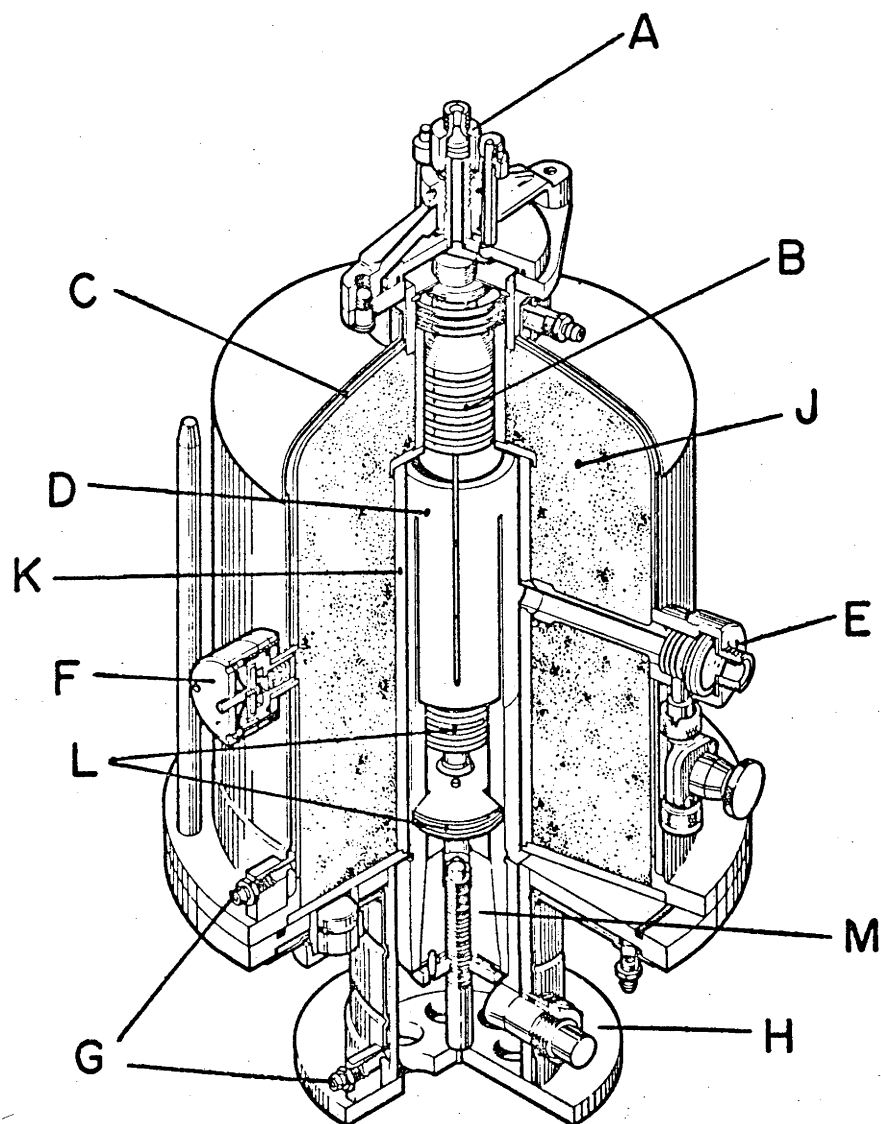


Figure 4.2. Diagram of Spemby furnace (graphite element version).

A - top sighting port; B - radiation shields; C - water jackets;
 D - graphite element; E - side sighting port; F - relief valve;
 G - hose adaptors; H - baseplate; J - graphite insulation;
 K - graphite liner; L - radiation shields; M - ceramic cone.

dust insulation. A sight tube was provided at the side, through the insulation and casing, so that the main graphite crucible could be viewed when in position in the hot zone. A removable loading port at the top included a second sighting facility and a hole through which a thermocouple could be sealed. The hood could be purged continually with a slow flow of argon (about 200 ml per minute) which entered near the side sighting port. The flow of gas away from the silica sighting window prevented condensation of graphite onto this window when running at very high temperatures.

In place of the top sighting port, a loading device could be fitted containing a chamber separated from the body of the furnace by a vacuum tight gate valve. This enabled diffusion couples to be lowered into the furnace when it was already at temperature. Several successive annealings could therefore be conducted without the need for cooling the furnace and repeating the preliminary procedure for every sample. Vacuum lines were fitted so that the loading chamber could be evacuated and purged with argon independently of the main furnace.

An alternative form of the furnace is shown in figure 4.3. In this case, no insulation was used inside the water-cooled hood and a Penning type ionisation gauge could be fitted. The electrodes, again water-cooled, were positioned vertically, supporting from the top an element made from tungsten strips riveted at either end to a tantalum former. A number of cylindrical radiation shields constructed from tantalum and molybdenum sheets encased the element to minimise heat losses to the base and hood. As before, provision was made for sighting the charge from both the top and the side and a channel in the top radiation shields permitted access to the hot zone for a thermocouple. The furnace in this form was capable of achieving 2400°C under 10^{-5} torr. Heat-up time was very rapid and this proved useful for preliminary temperature calibrations.

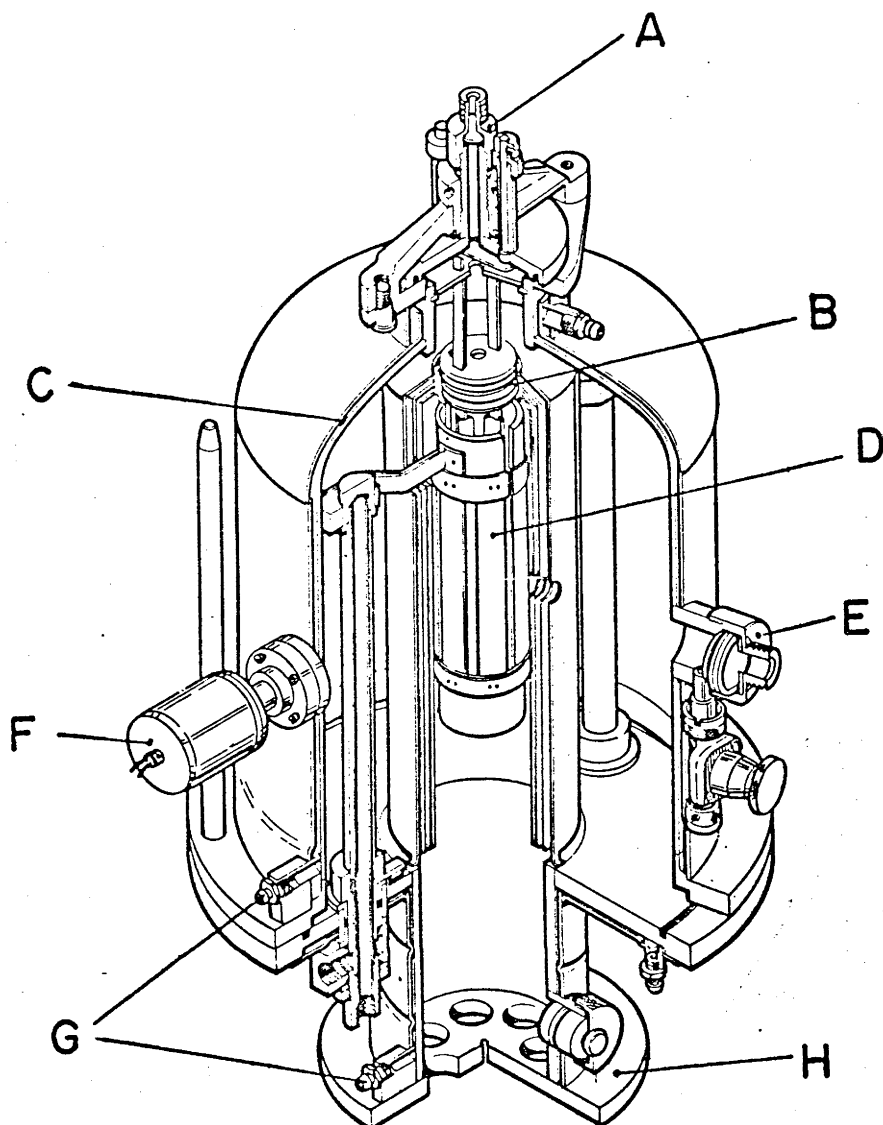


Figure 4.3. Diagram of Spembly furnace (tungsten element version).

A - top sighting port; B - radiation shields; C - water jackets;
D - tungsten element; E - side sighting port; F - penning gauge;
G - hose adaptors; H - baseplate.

To make accurate temperature measurements and to control the furnace temperature, an attachment was made to fit the side sighting tube which included a glass splitter set at 45° to the axis of the tube. Radiation passing directly through the splitter was used to measure the furnace temperature with a Leeds and Northrup optical pyrometer (type 8632-C) which had been calibrated by the National Standards Laboratory, Sydney. The fraction of the radiation turned through 90° was sensed by a silicon photocell (manufactured by Land). The e.m.f. output from this cell was fed to a proportional indicating temperature controller which regulated the amount of power required to maintain a pre-set temperature. The amplified output from this instrument was used as the control current for a saturable reactor supplying a maximum of 12 KVA at 25 V to the graphite or tungsten element via a transformer. Manual control was also possible using a continuously variable auto-transformer to control the current to the saturable reactor.

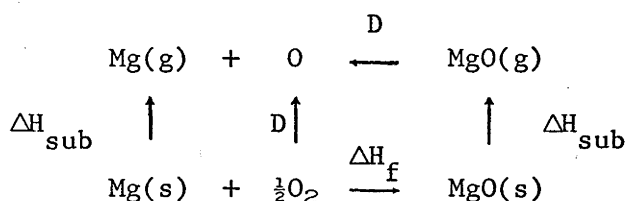
In practice it was found that the automatic proportional controller over-compensated when a relatively cold crucible was lowered into the hot zone. This overloaded the supply line. For this reason, manual control was preferred, particularly when working at very high temperatures (i.e. near maximum power). Furthermore, the equilibrium temperature could be achieved more rapidly in this manner. Good control was possible by continuously monitoring the output of the silicon photocell on a chart recorder. With practice, an accuracy of $\pm 5^{\circ}\text{C}$ could be maintained. This, in fact, was better than the calibration accuracy of the pyrometer.

4.3. Problems encountered at ultra-high temperatures

4.3.1. Evaporation of magnesium oxide

The various thermodynamic quantities involved in the

thermochemical cycle



have been reviewed by Schofield [1967] and Brewer and Rosenblatt [1969]. Details of the total vapour pressure of MgO and the composition of the vapour over a wide temperature range have been given by Kulikov [1966] and his data are reproduced in figure 4.4. It is apparent that, at the highest temperatures, evaporation occurs mainly to gaseous MgO. In any case, it is considered that equal numbers of Mg and O atoms are likely to leave the crystal surface at all temperatures, except when traps for electrons and holes are present in sufficient numbers (see section 3.2.5). We now consider the problem of loss of material from the surface layers of a diffusion couple, which could result in measured penetration distances that are too small.

A preliminary experiment was carried out to check the extent of weight loss of an MgO single crystal sample at 2000 °C in the graphite element-argon atmosphere form of the Spembyl furnace. The result is shown in figure 4.5 where percentage weight loss is plotted against time. The initial rapid loss was, presumably, due to a preferential evaporation from the edges of the cubic sample. After a period of about 40 minutes, the weight loss became linear with time and amounted to about 0.07% per minute. This was equivalent to the removal of about 0.3 μm per minute from the six faces of the cube. Since annealing times at this temperature were usually between 15 and 30 minutes, it was clearly desirable to reduce this loss of material. Furthermore, loss rates at higher temperatures could be expected to be

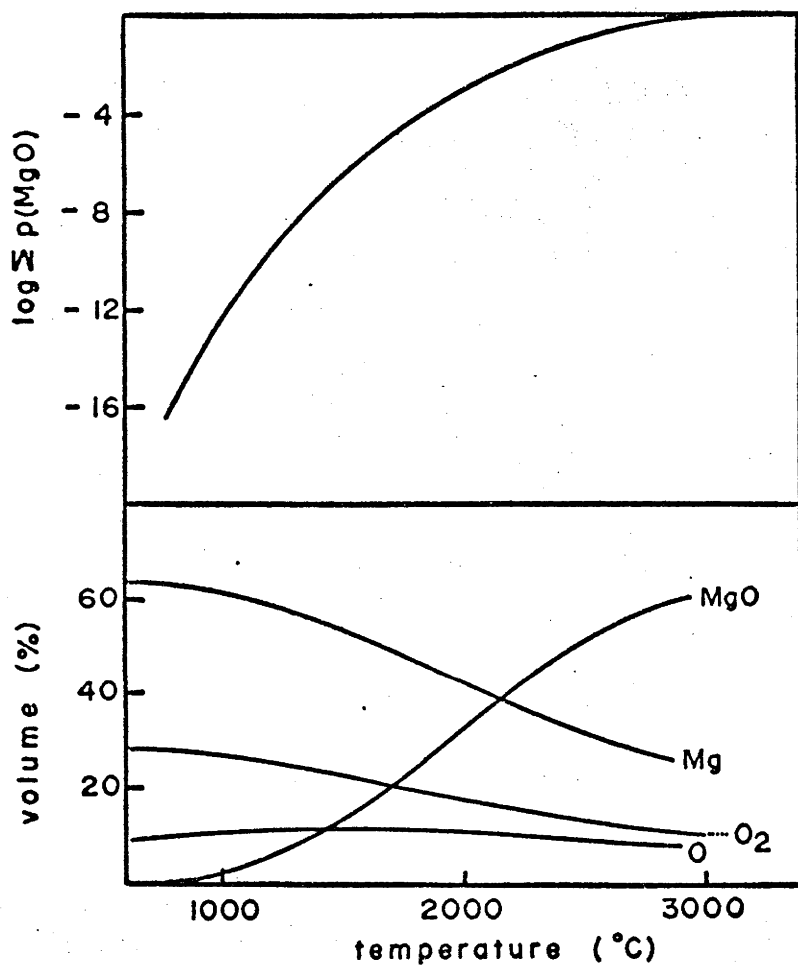


Figure 4.4. The total pressure of vapour and its composition in equilibrium with solid MgO for temperatures of 600 - 3000 °C [after Kulikov, 1966].

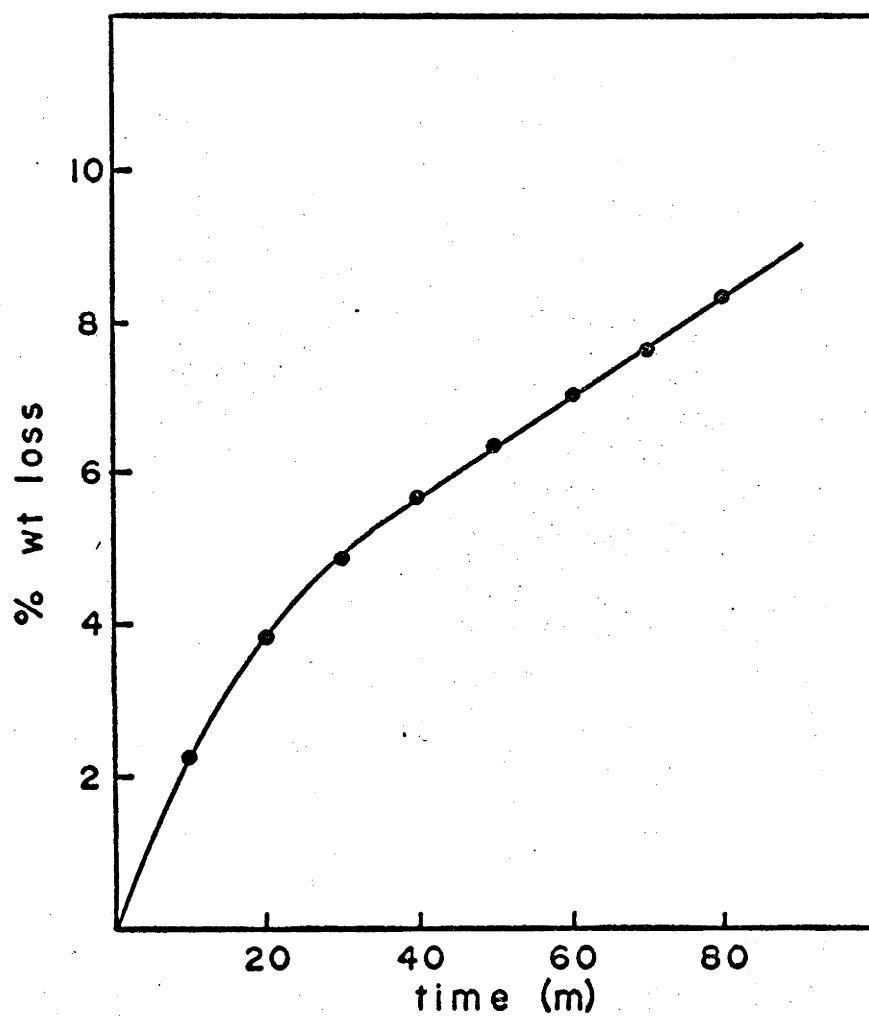


Figure 4.5. The rate of evaporation of MgO single crystal exposed to the reducing atmosphere of the Spembly furnace at 2000 °C.

considerably greater. The main reason for these evaporation rates was thought to be continuous vapour phase reduction in the non-equilibrium conditions created by the argon gas flow around the crystal. The prevention of this evaporation using the technique of embedding the single crystal in pressed MgO powder [Wuensch et al., 1972] was found to be impracticable, because the polycrystalline material shrank on sintering exposing the single crystal again. Therefore, containers were made, in which the diffusion couples could be placed, by cold pressing and sintering MgO powder.

The tool used is shown in figure 4.6. It consisted of a barrel with a removable base plate, and a piston. A 5° taper was machined into the base of the barrel and a relieving groove cut into the piston behind the pressing face to avoid jamming. Some preliminary drying and compacting of the MgO powder was necessary to increase the particle size. For the final pressing, about 30 grams of powder were loaded into the tool and subjected to a pressure of 10 tons per square inch. Higher pressures appeared to produce very little further decrease in volume. The base plate was then removed and the exposed pellet was drilled in situ to a depth of $\frac{5}{8}$ " using a tungsten carbide tipped drill. A recess was turned in the lip of the hole to take the container lid. This lid was produced in a similar manner using a smaller tool. After machining, the container was pushed from the barrel and, with the lid, was sintered in an argon atmosphere by heating to 1700°C over $1\frac{1}{2}$ hours, followed by a further one hour at this temperature. Considerable shrinking occurred, but by careful control of the pressing and sintering conditions, it proved possible to produce a sufficient number of containers and lids for the high temperature diffusion programme. After cooling and removal from the furnace, the lid was ground into the container to produce a close fit.

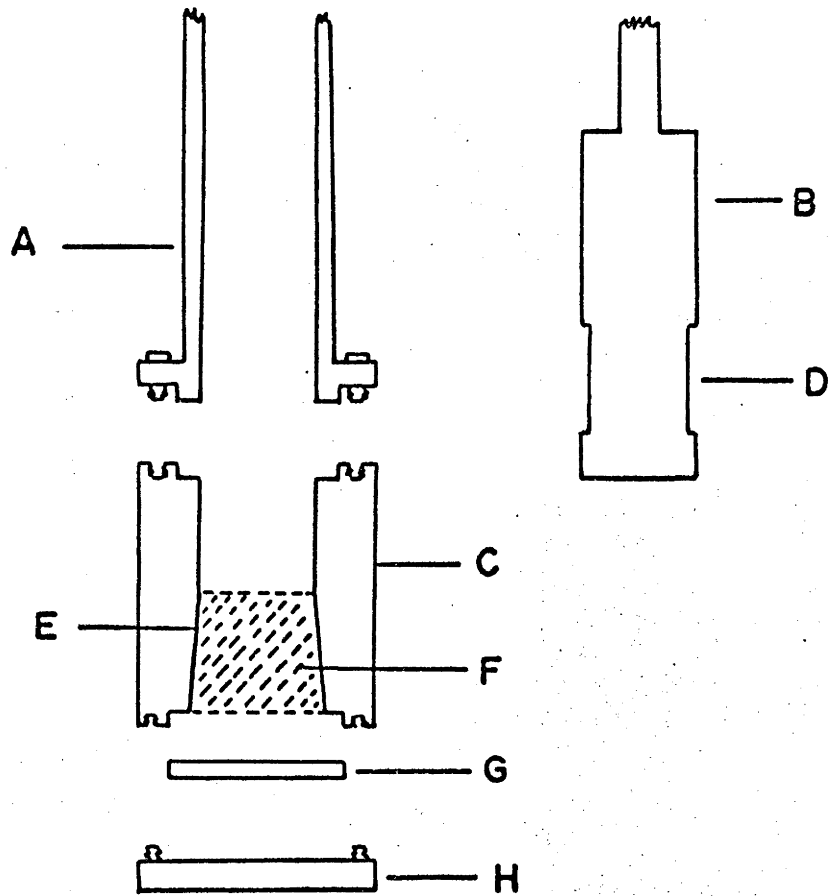


Figure 4.6. Tool for pressing MgO powder in the production of crucibles for high temperature diffusion studies.

A - extension tube; B - piston; C - barrel; D - relieving groove;
E - taper; F - MgO compact; G - spacer; H - baseplate.

The evaporation check was then repeated, again at 2000 °C, with the single crystal cube enclosed in the magnesia container just described. This time no weight loss was detectable (< 0.0001 gm). The same result was obtained even after ten minutes at 2640 °C. Using the highest vapour pressures reported for 2400 °C (4×10^{-2} atm.) and assuming equilibrium conditions existed inside the magnesia crucible, it was calculated that the evaporation of a layer only 40 Å thick over the surface of the crystal was sufficient to saturate the free space in the container. This also assumed that no vapour was contributed by the polycrystalline container itself. Naturally, the equilibrium between the crystal and its surroundings was dynamic in nature, but it was considered safe to conclude that the effect of vaporisation on diffusion profiles could be neglected, provided that there was a good fit between the magnesia container and its lid.

4.3.2. Preliminary temperature checks

The arrangement used for temperature checks in the Spemby furnace is shown in figure 4.7. A magnesia crucible was placed inside the main graphite crucible (to be used when lowering samples into the hot furnace during actual diffusion runs) supported on a graphite block inside the furnace element. A hole drilled in this block to a depth of about six times its diameter ($\frac{1}{8}$ ") was arranged so that it could be viewed from the side sighting window with a pyrometer. Such a hole can be regarded as a black body radiator. The cap of the magnesia container was left off and inside was placed a segment of graphite, which could be used as a target for temperature measurements from the top sighting window. A thermocouple was inserted through the top of the furnace hood and its tip placed adjacent to this graphite segment.

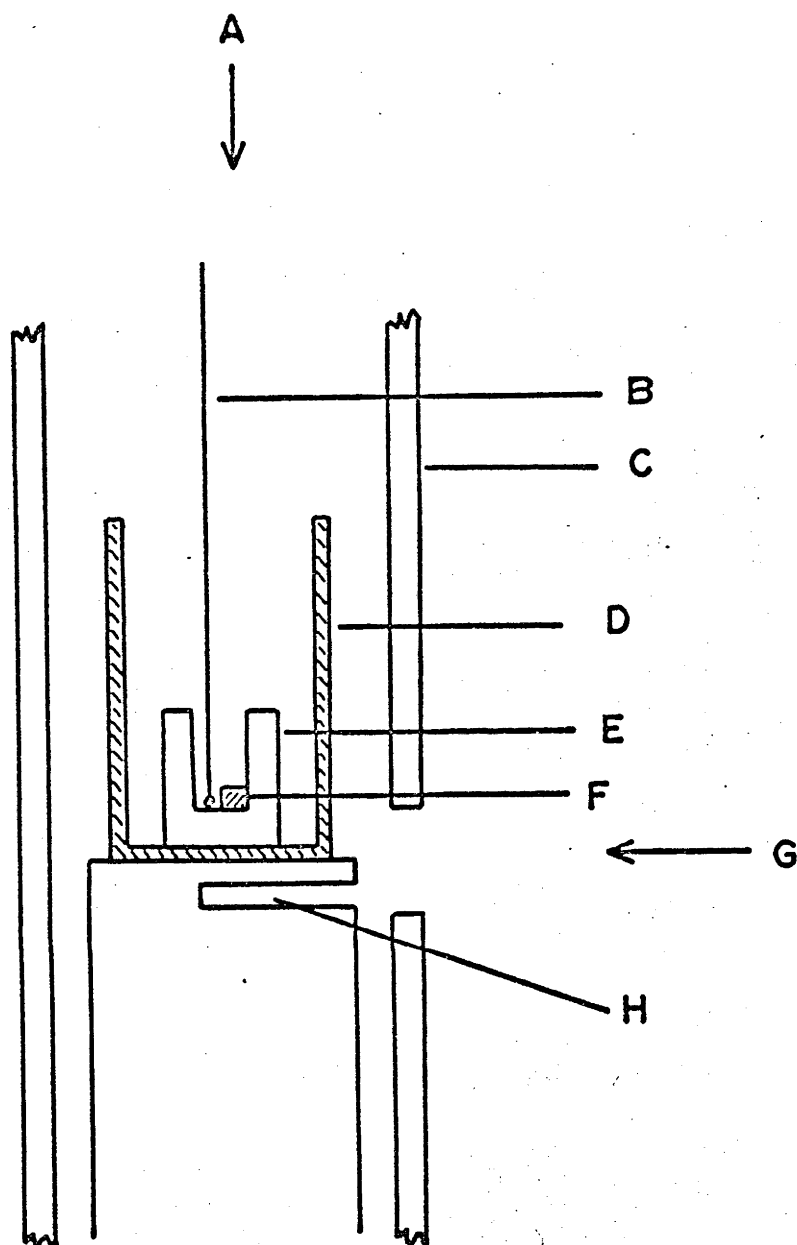


Figure 4.7. Crucible and target arrangement used for temperature checks and calibration at very high temperatures.

A - top sighting port; B - thermocouple ($< 1600^{\circ}\text{C}$); C - graphite element; D - graphite crucible; E - MgO crucible; F - graphite target segment; G - side sighting port; H - 'black body' hole in graphite.

The 'A' value of a pyrometer absorption screen is a constant value such that if T_1 and T_2 are, respectively, the high and low range absolute temperatures corresponding to a particular setting of the pyrometer, then

$$A = \frac{1}{T_2} - \frac{1}{T_1} . \quad (4.14)$$

This formula was used to determine the correction factors for the silica sighting windows and the 45° glass splitter (for 'straight-through' viewing). The mean values obtained were $(3.0 \pm 0.3) \times 10^{-6}$ and $(5.7 \pm 0.2) \times 10^{-6}$ reciprocal degrees, respectively. The correction for the emissivity of the graphite obtained by sighting the pyrometer on the exterior of the block (or crucible) was only a few degrees. An 'A' value for this appeared to remain constant within the accuracy of the pyrometer and was equal to $(2.2 \pm 0.2) \times 10^{-6}$ reciprocal degrees.

Next, temperature readings of the inside of the magnesia crucible, using the top sighting port and the graphite segment as target, were compared with readings obtained from a Pt - Pt/18% Rh thermocouple adjacent to the segment. At the same time, the temperature of the exterior of the graphite crucible was read through the side sighting port. Above 1600°C the thermocouple was abandoned, but the pyrometer readings were continued up to 2500°C . The discrepancy between the thermocouple temperature and that measured by the pyrometer agreed with the correction found necessary by the National Standards Laboratory. Therefore, the thermocouple readings were regarded as accurate. From this, and allowing also for the difference between readings on the 'high' and 'extra-high' ranges of the pyrometer, it was possible to construct a graph from which the temperature inside the magnesia crucible could be derived from the reading of the pyrometer sighted on the exterior surface of the graphite crucible. This

calibration is shown in figure 4.8. (Note that the uncorrected pyrometer reading through the side sighting port was very nearly equal to the true temperature inside the magnesia crucible.)

The final check required was to determine the difference, if any, between the heat-up curves for the interior and the exterior of the crucibles. Since this again required the use of both sighting ports, the loading rig could not be used. Therefore the graphite element and insulation were replaced by the tungsten element and its radiation shields. With the crucibles in place, a rapid heat-up could be achieved in this arrangement, simulating the conditions at the start of a diffusion annealing when the sample, inside the magnesia crucible, was lowered into the already hot furnace. Figure 4.9 shows that there was no significant difference in the heat-up times for the inside and the outside of the crucibles, and hence the annealing time for a diffusion run could be corrected satisfactorily using the exterior heat-up curve.

4.4. Experimental method

4.4.1. General procedure

The Monocrystals cylinders of single crystal MgO did not cleave easily and each was cut into approximately equal pieces using a 0.006" diamond wheel. The faces exposed were then polished using 9-1 μm diamond paste on plate glass. This removed the worst of the damage and produced a sufficiently flat surface on which to deposit the tracer. The Ventron MgO cleaved readily from the pieces supplied into approximately 3-4 mm cubes. The faces were clean and flat. One face of each was polished with 1 μm diamond paste to remove the cleavage 'rivers' and the tracer was deposited on this face using a micro-syringe. Deposition (0.02 ml) was carried out in the presence of

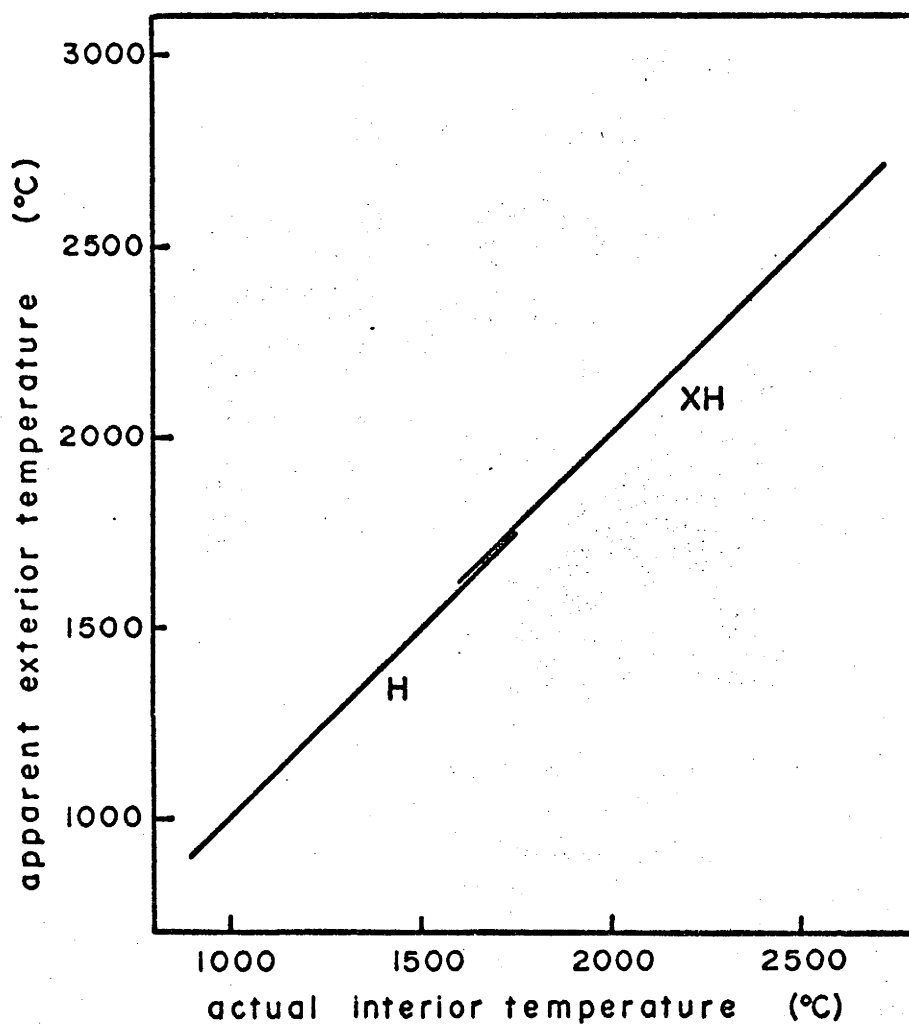


Figure 4.8. Graph used to determine the temperature of the MgO crucible interior from that of the graphite crucible exterior.

H - 'high' range; XH - 'extra high' range.

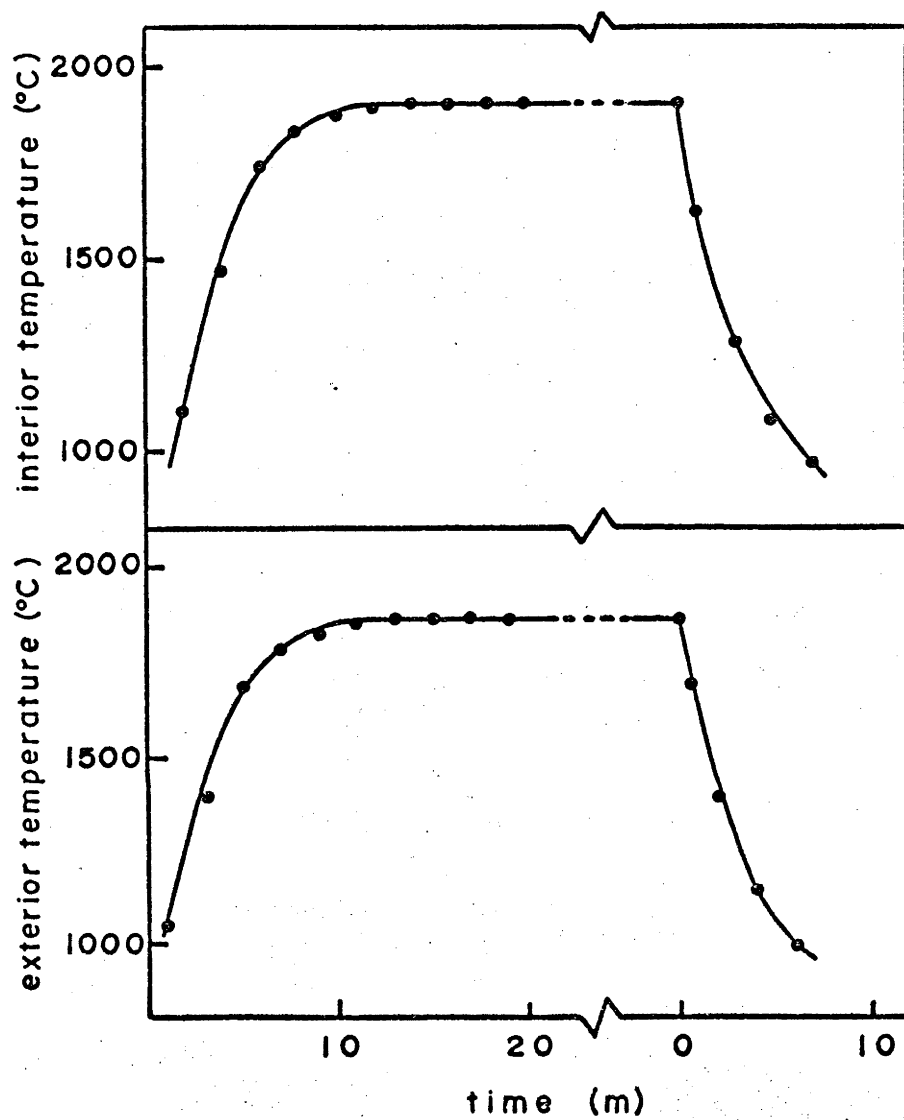


Figure 4.9. Simultaneous heat-up and cooling curves for the MgO crucible interior and the graphite crucible exterior.

ammonia vapour to promote the precipitation of hydroxide and conversion to oxide on drying and heating. The deposit was dried under an infra-red lamp and pairs of crystals were bound together using a loop of Pt - Pt/13% Rh wire to form diffusion 'sandwiches'. This helped to reduce the tracer lost during annealing.

For annealing up to 1750 °C in platinum wound furnaces, the sandwich was contained in a high purity alumina tube. This tube was lowered slowly into the hot zone of the furnace and a thermocouple (Pt - Pt/10% Rh) placed with its tip in contact with the sample. A brass seal was made to fit over the open end of the tube to prevent the possible escape of radioactive material. In some experiments, the tube was purged slowly (50 ml per minute) with argon. Couples were annealed between 1000 °C and 1750 °C for periods ranging from one hour to several weeks. Temperatures were controllable to ± 2 °C. In one or two cases, there was a tendency to drift over the duration of the experiment where this was lengthy, but with regular checking using the potentiometer, this could be corrected before it became serious. The error in the annealing time was negligible in these experiments since heating took only a few minutes. Cooling on withdrawal from the furnace was very rapid also.

For the ultra-high temperature experiments, it was found necessary to pre-anneal the diffusion couples, usually for periods ranging from one hour at 1200 °C for self-diffusion where time was important, to 100 hours at 1000 °C. This helped to 'fix' tracer in each crystal surface and prevented tracer loss on rapidly heating the couple in the Spembyl furnace. After pre-annealing, the binding wire was removed from the couple which was then placed in a magnesia crucible. The cap was placed in position and the whole put inside the main (open) graphite crucible, which was suspended by means of a

tantalum chain and steel wire in the loading chamber at the top of the furnace. The loading chamber was sealed, evacuated and purged with argon. The furnace, having been similarly purged, was brought to the required temperature, the gate valve between the furnace and the loading chamber opened and the crucible carefully lowered. The arrival of the charge in the hot zone was indicated by a rapid fall in the output from the silicon photocell as indicated on the chart recorder. At this moment, the timer was started and pyrometer readings of the crucible temperature were recorded to obtain a heat-up curve. Manual adjustments were made to bring the sample to a steady temperature as quickly as possible. This temperature was obtained from the calibration curve, figure 4.8. Annealing times ranged from ten minutes to several hours. The sample was then withdrawn into the loading chamber, isolated, and allowed to cool.

The annealing time was corrected where necessary from a heat-up curve such as that shown in figure 4.10. Assuming that no significant diffusion occurred below a temperature at which D was 10% of the expected value at the final steady temperature, the time zero (t_0) was taken as the point such that the shaded areas in figure 4.10 were equal.

A diffusion sandwich, on being removed from the furnace, was separated into its two halves. All faces of each half (other than the diffusion face) were ground away, using 400 grit carborundum paper, to a depth of about $10\sqrt{Dt}$. This ensured that no contribution to the sample activity could arise from contamination or surface diffusion. After cleaning, the crystal was mounted on the grinder using the mounting plastic as described earlier. The crystal was first counted to determine its total activity, a thin layer of material removed by polishing with 1 μm diamond paste, the grinder immersed in a water bath

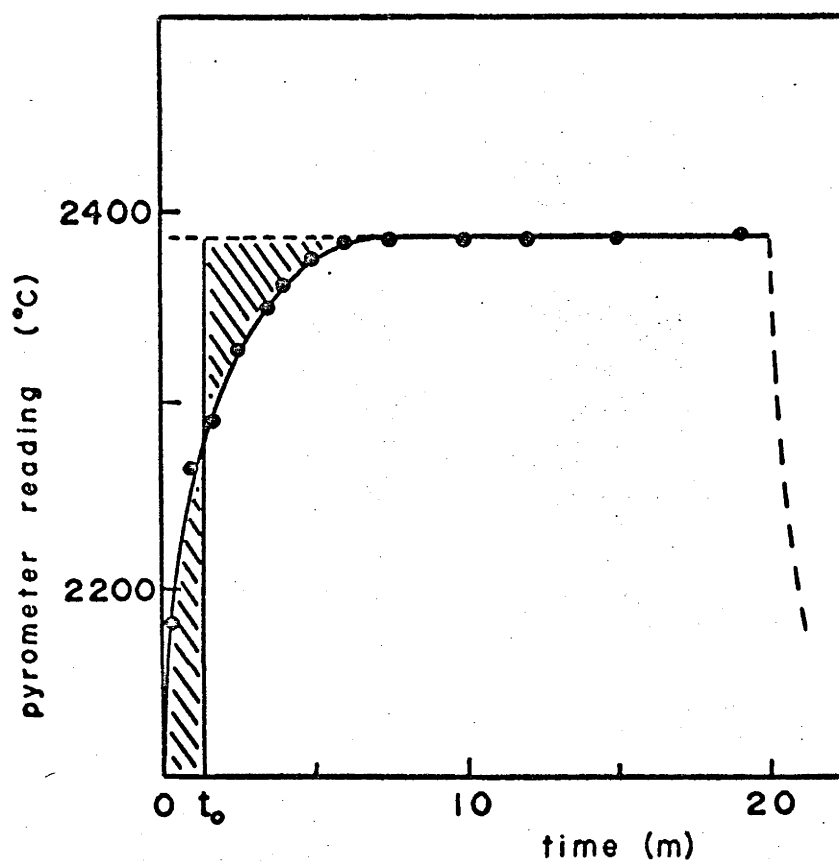


Figure 4.10. Typical heat-up curve for a diffusion run showing the method of correcting the annealing time, t .

to restore it to its initial temperature, the amount removed measured using a dial gauge and the crystal activity determined again. The background and standard source were checked at regular intervals to correct the activity remaining, $A(x)$, which was then plotted against the penetration distance, x . The diffusion coefficient, D , was then evaluated as described in section 4.1.

4.4.2. Comments on specific experiments

(i) An analysis of the tracer solution used in the first self-diffusion experiments showed the presence of 2000 $\mu\text{g/ml}$ of Al^{3+} . The presence of this impurity in fact proved fortunate, because it extended the extrinsic region over a much wider temperature range than it would otherwise have covered. Thus two sets of diffusion experiments were performed, one using undiluted, as-received Mg-28 tracer and the other using tracer diluted twenty times to reduce the Al^{3+} impurity to levels below the 'grown-in' impurity content of the single crystals. The temperature range covered in both sets of experiments was about 1150 $^{\circ}\text{C}$ to 2350 $^{\circ}\text{C}$. During early high temperature experiments in the Spembyl furnace, results suggested that evaporation of both tracer and host material occurred more readily in self-diffusion experiments than in impurity diffusion runs. A trace (1 μg) of Ca^{2+} added to the Mg-28 solution deposited on each sample appeared to reduce this volatility [cf. Somorjai, 1969], although in some cases it made the original $x = 0$ plane somewhat indistinct. Beyond 2350 $^{\circ}\text{C}$, it proved impossible to counter the effects of evaporation as could be seen from the highly glazed surfaces resulting from heating to such temperatures. Mg-28 has three major γ peaks at 0.40 MeV, 0.95 MeV and 1.35 MeV and all three were counted in order to minimise counting times. For γ energies in this range, absorption of the radiation in MgO over the penetration

distances involved was negligible [Harding, 1967b]. The tracer was checked for radioactive impurities by measuring its half-life, which was found to be in agreement with the published value of 21.3 hours over at least ten half-lives. However, as a precaution, no work was done beyond a period of six half-lives with any given batch of tracer.

(ii) Nickel-63 is a soft β radiator (0.067 MeV) and the absorption coefficient was calculated to be 5000 cm^{-1} in MgO. An ORTEC end-window detector was used in this work. Annealing temperatures covered the range 1100°C to 2500°C . Up to 1700°C runs were carried out in argon as well as air to check for a possible atmosphere effect. Unfortunately with the equipment available it was not possible to anneal samples in air above this temperature. In addition, several experiments were performed in the range 1500°C to 1900°C with Al^{3+} added to the tracer to simulate the conditions under which the early self-diffusion studies had been done.

(iii) Barium-133 diffusion in MgO had already been studied [Harding, 1967a, 1967b] up to 1700°C . However, several runs were repeated in this temperature range under an argon atmosphere, and additional data for air annealing were collected in the temperature range 1500°C - 1700°C . The upper limit of the measurements was extended to 2450°C . This tracer has a major γ peak at 0.36 MeV and again no correction was necessary for absorption. Some diffusion profiles, even up to 2000°C , showed evidence of a second region reported in the earlier work. In order to investigate this further, the following experiments were performed. A total of twelve MgO cubes of about 3 mm side were pre-annealed in air at 1580°C , after one face on each had been polished in the usual manner, for times ranging from 0 to 94 hours. Six couples were then made up and diffusion annealed in air for 1 hour, again at 1580°C . In this way, the effect of pre-annealing on the damage

responsible for the profile shapes, could be determined.

(iv) Another impurity that was considered to be of interest from the diffusion point of view was beryllium. With an ionic radius of about $0.35 \text{ \AA}$, this ion is small enough to fit interstitially into the MgO lattice with the minimum of strain. Earlier studies [Harding and Mortlock, 1966] showed that the diffusion coefficients measured in the range $1000\text{--}1700^\circ\text{C}$ were larger than those determined for other ions. These measurements were repeated and extended up to 2350°C .

(v) Both Cd^{2+} and Ca^{2+} have the same ionic radius (about $0.98 \text{ \AA}$) and therefore a study of the diffusion of these ions in MgO was made in order to determine the effect, if any, of polarisability. Measurements were made only in the temperature range $1850\text{--}2400^\circ\text{C}$ where the effect of impurities and structural damage could be avoided. In the case of cadmium, the chloride was found to be rather volatile and hence ion exchange was used to convert it to the fluoride [Harding and Bhalla, 1971]. This together with the ammonia technique, reduced the amount of tracer lost on initial heating. Pre-annealing temperatures were reduced to 800°C for the same reason. Cd-115m is an energetic β radiator (1.6 MeV) and absorption in MgO was found to be negligible in these experiments, with $\mu = 30 \text{ cm}^{-1}$ (see figure 4.11). However, analysis of the experimental data for Ca^{2+} proved to be more complex since for Ca-45, μ was found to be in the intermediate range at 430 cm^{-1} (see figure 4.12).

(vi) The final tracer used in these diffusion studies was Ge-68. This decays with a 270 day half-life to Ga-68 by K capture. The daughter further decays by positron emission with a half-life of 68 minutes. Thus, allowing sufficient time after annealing, usually 24 hours, a concentration profile for germanium in MgO could be determined by counting the gallium annihilation radiation (0.51 MeV). Germanium

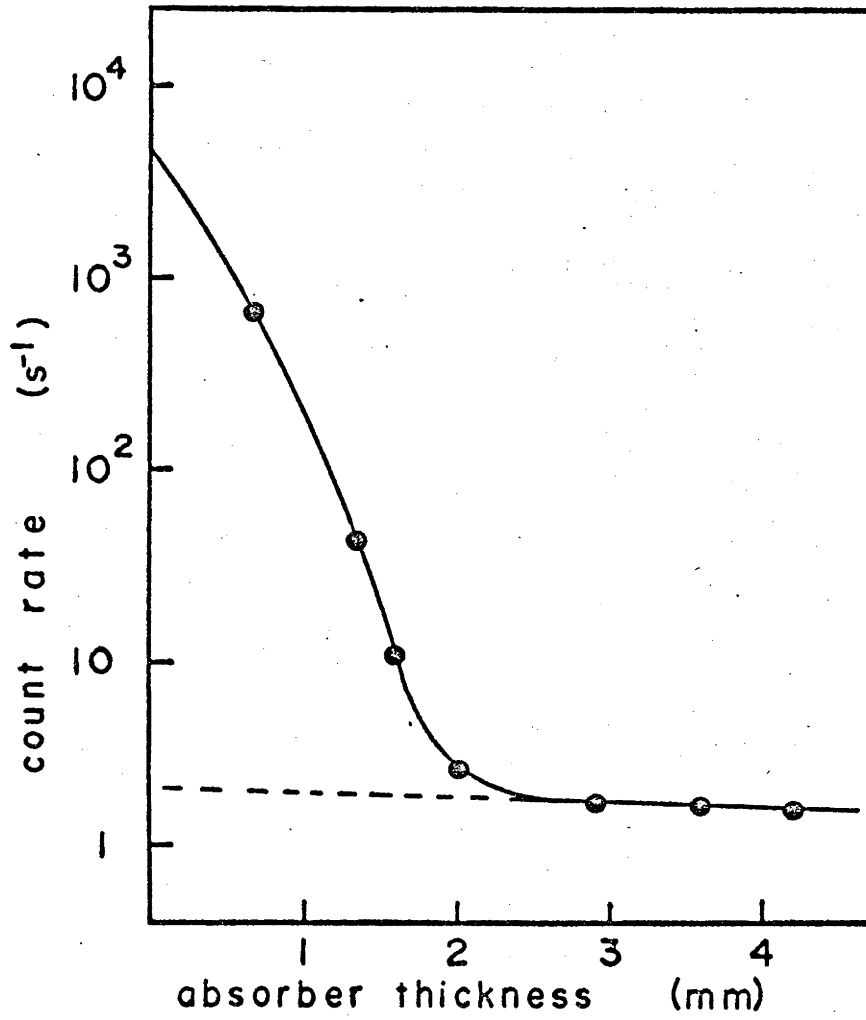


Figure 4.11. Absorption of Cd-115m β -radiation in single crystal MgO ($\mu = 30 \text{ cm}^{-1}$).

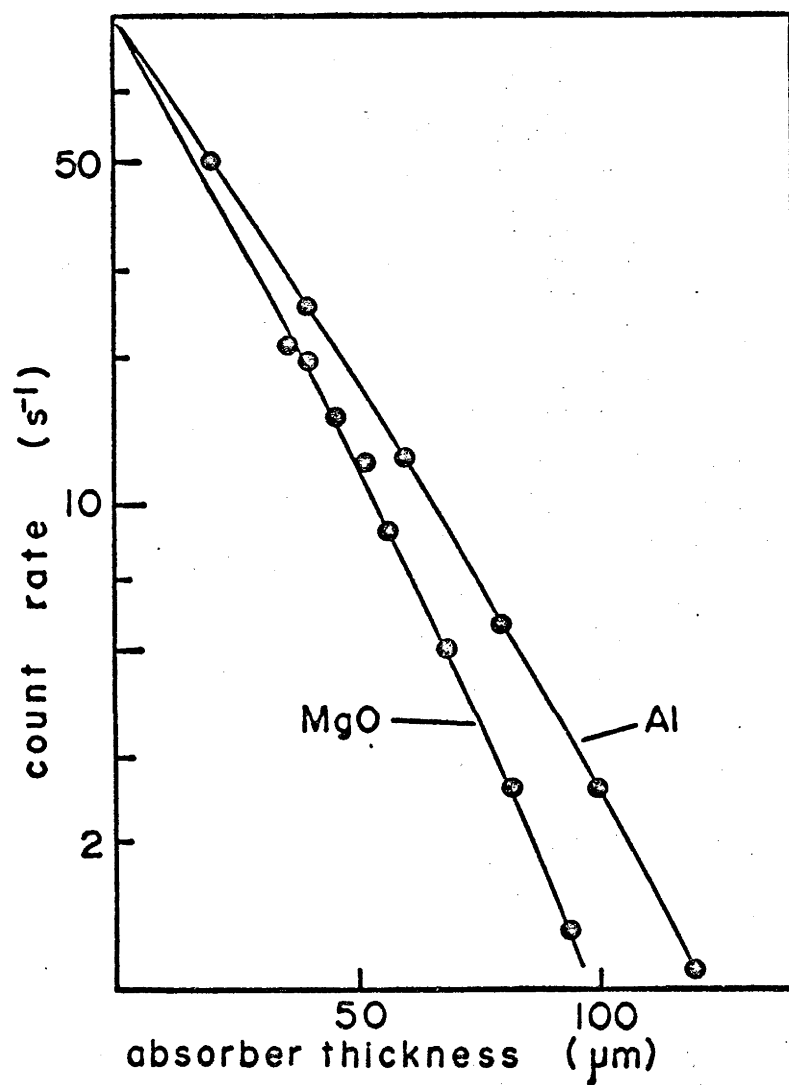


Figure 4.12. Absorption of Ca-45 β -radiation in single crystal MgO ($\mu = 430 \text{ cm}^{-1}$) and aluminium.

can exist either as Ge^{2+} or Ge^{4+} and it was considered that a comparison of diffusion data for this ion with that for the divalent ions in the temperature range 1850-2350 °C might permit a decision to be made concerning the valence state of germanium in the MgO lattice. However, a full investigation of the effect of ionic charge on diffusion parameters was not seen as part of this project.

4.5. Sources of error in the measurement of D

4.5.1. Boundary conditions

Mortlock [1964, 1969] has discussed a possible error arising from the use of an incorrect solution to the diffusion equation for the analysis of experimental results. Solubility data, even if available, do not always assist in deciding whether equation (2.5) or equation (2.6) should be used, since such data apply to an equilibrium situation. It is quite possible that a normally soluble impurity deposited on the surface of an MgO single crystal has insufficient time to dissolve completely, particularly when annealing times are short. Usually, in this work, the presence of an excess of tracer at the crystal surface after annealing was obvious from the large difference in count rate observed before and after the first abrasion was made. Often this excess could be seen with the eye on close inspection. Under these conditions, equations (2.6) and (4.7) are applicable, but should equations (2.5) and (4.5) be applied in error, the graph of $\text{erfc}^{-1} F(x)$ vs. x would still be an approximate straight line, with a negative intercept on the x -axis. If this line is not forced through the origin as Mortlock's calculation of the resulting error in D assumes, the slope would not differ greatly from that of the correct $\text{ierfc}^{-1} F(x)/1.772$ vs. x plot. It is interesting to note, however, the conclusion drawn by Mortlock, that at small penetrations, the residual activity method of profile

analysis used here yields much smaller errors due to the application of incorrect boundary conditions than the commonly used method based on the direct determination of concentration as a function of penetration distance, x .

4.5.2. Location of the original crystal surface

It was noted in many results that graphs of $\operatorname{erfc}^{-1} F(x)$ (equation (4.5)) and $\operatorname{ierfc}^{-1} F(x)/1.772$ (equation (4.7)) vs. x , and $\log f(x)$ vs. x^2 (equation (4.12)) did not pass through the origin, but showed a positive intercept on the x -axis. This could have been due to a layer of porous undissolved material at the surface rendering the true $x = 0$ plane uncertain, particularly in cases of low impurity solubility or where annealing times were short. A second possible explanation is that a thin layer of surface damage, produced by diamond polishing during preparation of the diffusion sandwich, was present. This problem has been studied by Koepke and Stokes [1970], and it could give rise to a region of very rapid diffusion in the first 1-5 μm of the diffusion zone. These explanations are consistent with the fact that the first section was generally more easily removed than subsequent sections, i.e. the surface material appeared to be softer than the bulk of the crystal. Another cause of a positive x -intercept could be the possible presence of aliovalent impurity ions in the tracer solution (as was found in the case of the Mg-28 used in the self-diffusion experiments) or the influence of OH^- ions in the surface region. Both could give rise to a higher than normal concentration of cation vacancies and hence a higher diffusion rate in the first few microns.

At very high temperatures, additional factors may cause errors in the location of the $x = 0$ plane. In some samples, a region

of reduced activity was found near the surface. Wuensch and Vasilos [1971] who also encountered this phenomenon, attributed it to the loss of solute towards completion of a diffusion annealing, and the subsequent reverse diffusion of tracer out of the specimen. This would have been possible in the experiments reported here, in spite of the pre-annealing procedure, if the containing crucible had cracked due to thermal shock, or otherwise developed a leak exposing the diffusion couple to the argon flow. Occasionally, evaporation of the single crystal itself occurred as could be seen from the highly glazed sample surfaces. These runs were abandoned.

Whatever the cause of these surface anomalies, it was assumed that diffusion coefficients evaluated from data well within the crystal were not affected. Where a thin residual deposit could be seen, the $x = 0$ plane was taken to be the point at which it vanished as sections were carefully polished away.

4.5.3. The calculation of D

Diffusion coefficients were evaluated from the slopes of the graphs of $\operatorname{erfc}^{-1} F(x)$ vs. x , $\operatorname{ierfc}^{-1} F(x)/1.772$ vs. x , or $\log f$ vs. x^2 , as explained previously. The errors in the calculation of these slopes must therefore be considered. The functions $\operatorname{erfc}^{-1} u$ and $\operatorname{ierfc}^{-1} u$ are plotted against u in figure 4.13. For experiments to which equation (4.5) was applicable, $u = F(x)$, and we can write

$$[\operatorname{erfc}^{-1} F(x)] = \frac{d[\operatorname{erfc}^{-1} F(x)]}{d F(x)} F(x) . \quad (4.15)$$

For values of $F(x)$ greater than 0.2, $\operatorname{erfc}^{-1} F(x)$ vs. x is roughly linear and the slope is approximately unity. The error in $\operatorname{erfc}^{-1} F(x)$ is therefore the same as the error in $F(x)$. For $F(x)$ less than 0.2, the slope of $\operatorname{erfc}^{-1} F(x)$ vs. $F(x)$ increases rapidly and the error in

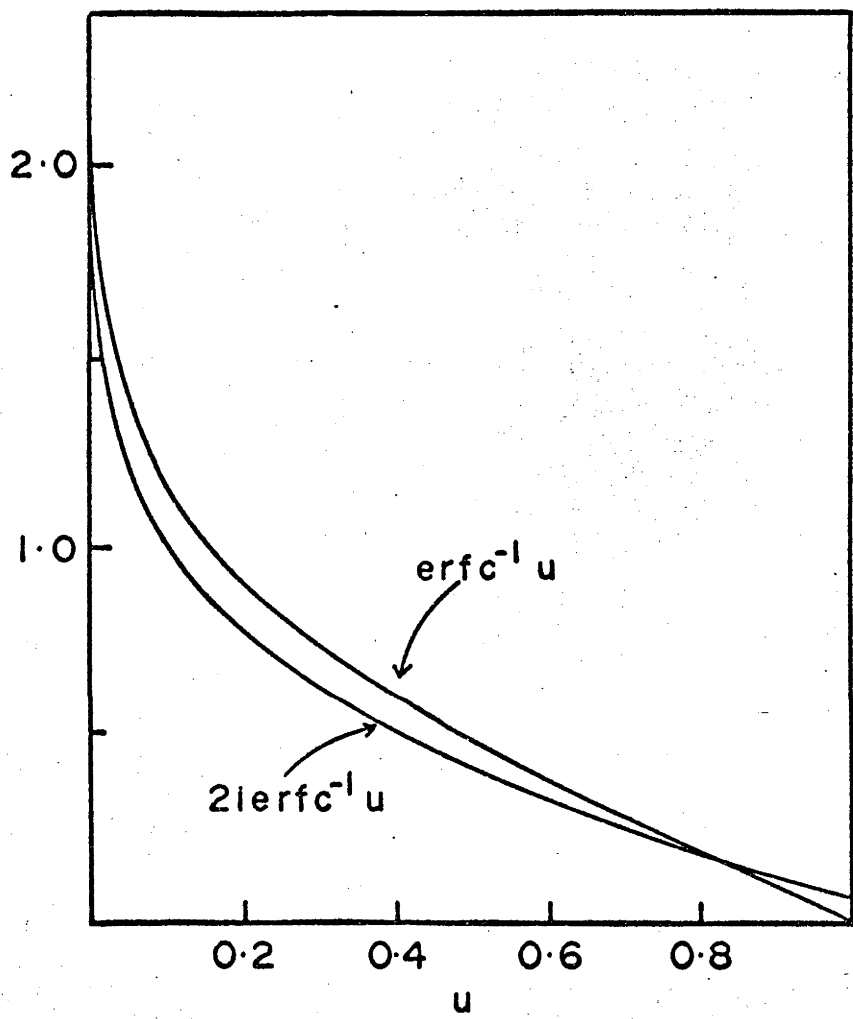


Figure 4.13. The functions $\text{erfc}^{-1} u$ and $2\text{ierfc}^{-1} u$ plotted against u .

$\text{erfc}^{-1} F(x)$ becomes very large for small $F(x)$ values. A small value of $F(x)$ corresponds to large penetrations, where counting errors, including background variations, and possibly short-circuit influences (dislocations and cracks) become significant. In practice, therefore, points on the $\text{erfc}^{-1} F(x)$ vs. x graph for $\text{erfc}^{-1} F(x)$ greater than 1.2 were regarded with some caution in many experiments. By reference to figure 4.13 a similar argument can be applied to results where equation (4.7) was used to determine D . The logarithmic plot also gives increasing errors as $f(x)$ decreases. Therefore, it was essential to minimise counting errors by accumulating sufficient counts. Individual measurements of sample activity were accurate to 2% or better. Usually at least 10,000 counts were collected, but in some instances where tracer solubility was low, it was necessary to reduce this to 3000. The error in $A(o)$ was similarly 1-2% when the $x = 0$ plane was well-defined. When this was not so, some estimation of its location was necessary with the aid of careful sectioning. The resulting error in $A(o)$ could then be as high as 10%. In practice, the effects on D of errors in the location of the original diffusion face and in $A(o)$ tended to cancel each other. Wuensch and Vasilos [1961] also found D to be relatively insensitive to $A(o)$. The error in $F(x)$, and hence in $\text{erfc}^{-1} F(x)$ or $\text{ierfc}^{-1} F(x)/1.772$, was therefore usually in the range 4-12%.

The other factor contributing to the error in the slopes from which D was calculated was the penetration distance, x . Errors arising from temperature variations of the grinder and dial gauge were minimised by performing the measurements in an air-conditioned room and immersing the grinder piston in a water-bath at this room temperature for several minutes after handling. A mean of several readings of the dial gauge over the sample surface gave each measurement to $\pm 0.3 \mu\text{m}$.

Since distances were obtained by subtraction, the error in the average penetration distance of 20 μm was therefore $\pm 3\%$. At very low temperatures, penetrations were lower and errors correspondingly increased.

The error occurring in the calculation of the appropriate slope, then, was typically in the range 7-15%. In addition, errors arose from time and temperature measurements. Where annealing times were long, errors were negligible, but at the shortest times, they could be as high as 10%. The effect of temperature errors on D can be determined as follows. We have

$$D = D_0 \exp(-\epsilon/kT) . \quad (4.16)$$

Hence

$$\Delta D = \frac{D_0 \epsilon}{kT^2} \exp(-\epsilon/kT) \Delta T \quad (4.17)$$

or

$$\frac{\Delta D}{D} = \frac{\epsilon}{kT} \frac{\Delta T}{T} . \quad (4.18)$$

Below 1700 $^{\circ}\text{C}$, the furnace temperature could be measured and controlled to better than 1 $^{\circ}\text{C}$. However, because of temperature gradients in the hot zone, ± 2 $^{\circ}\text{C}$ represents a more realistic limit. The resulting error in D is then 2-4% depending on T and ϵ . Above 1700 $^{\circ}\text{C}$, the measurement of temperature involved the use of the pyrometer. Readings were estimated to be accurate to ± 15 $^{\circ}\text{C}$ after considering control, calibration and reading errors. For $\epsilon = 3.3$ eV, the error in D would have been $\pm 15\%$ to $\pm 6\%$ over the temperature range 1700-2500 $^{\circ}\text{C}$.

A summary of errors is given in table 4.3 and the total error in individual diffusion coefficients was estimated to be 15-35%.

Table 4.3. Summary of errors contributing to the error in individual diffusion coefficients

Source of error	Magnitude	Effect on D
Slope of erfc^{-1} , ierfc^{-1} graphs (including counting and penetration errors)	7-15%	14-30%
Annealing time ($< 1700^{\circ}\text{C}$)	± 2 m	$< 3\%$
" " ($> 1700^{\circ}\text{C}$)	± 1 m	3-10%
Annealing temperature ($< 1700^{\circ}\text{C}$)	$\pm 2^{\circ}\text{C}$	2- 4%
" " ($> 1700^{\circ}\text{C}$)	$\pm 15^{\circ}\text{C}$	6-15%
Total error ($< 1700^{\circ}\text{C}$)		15-30%
" " ($> 1700^{\circ}\text{C}$)		15-35%

4.5.4. Errors in the Arrhenius equation

The method of least squares was used to determine the lines of best fit through data points on the $\log D$ vs. $1/T$ graphs, and errors quoted for activation energies and pre-exponential factors are standard errors. This procedure is not strictly correct because of the logarithmic plot and the invalid assumption that the error in $1/T$ is negligible. It is, however, a method commonly used to ensure a consistent assessment of data.

The factors causing errors in individual D 's discussed in the previous sections did not take into account the variation from sample to sample of the concentration of grown-in impurities. These variations are particularly important in the extrinsic region. In the intrinsic region, this is no longer significant, but errors in temperature become more pronounced and this, combined with the relatively narrow range of $1/T$ values, leads to errors in ϵ of about 10%.

5. Results

5.1. Cation self-diffusion in MgO

In section 4.4.2, it was pointed out that the Mg-28 tracer solution used in the self-diffusion studies contained aluminium as an impurity. The results therefore fall into two categories, those obtained with as-received tracer (referred to as ART results) and those for experiments using tracer diluted by a factor of twenty (DT results). The penetration of Mg-28 into MgO single crystals is shown in figure 5.1, where $\operatorname{erfc}^{-1} F(x)$ is plotted against x (equation (4.5)) for diffusion couples annealed under various conditions. Recently published data on inter-diffusion in the $\text{MgO-Al}_2\text{O}_3$ system [Whitney and Stubican, 1971] indicate that aluminium diffuses rapidly in MgO. From an analysis of the tracer solution, it was calculated that the mole fraction of Al^{3+} in the magnesium deposited on each sample could have been as high as 0.15, although it is uncertain how much of this would have been lost by evaporation or other means. The inter-diffusion results suggest that, under these conditions, the Al^{3+} penetration could have been as high as 500 μm after only two hours annealing at 1650 $^\circ\text{C}$, for example. The Mg-28 penetration at this temperature was only 50 μm (line 'D' in figure 5.1) over which distance the free vacancy concentration would not have varied greatly. This would have been so particularly if the degree of Al^{3+} -cation vacancy association increased towards higher Al^{3+} concentrations. The work of Solaga and Mortlock [1970] shows that this also applies to Sc^{3+} diffusion in MgO, since the penetration plots for this tracer are almost linear up to $\operatorname{erfc}^{-1} F(x) = 1.0$, for all concentrations of scandium. Therefore, in most cases, the $\operatorname{erfc}^{-1} F(x)$ vs. x graphs for Mg-28 in MgO were good straight

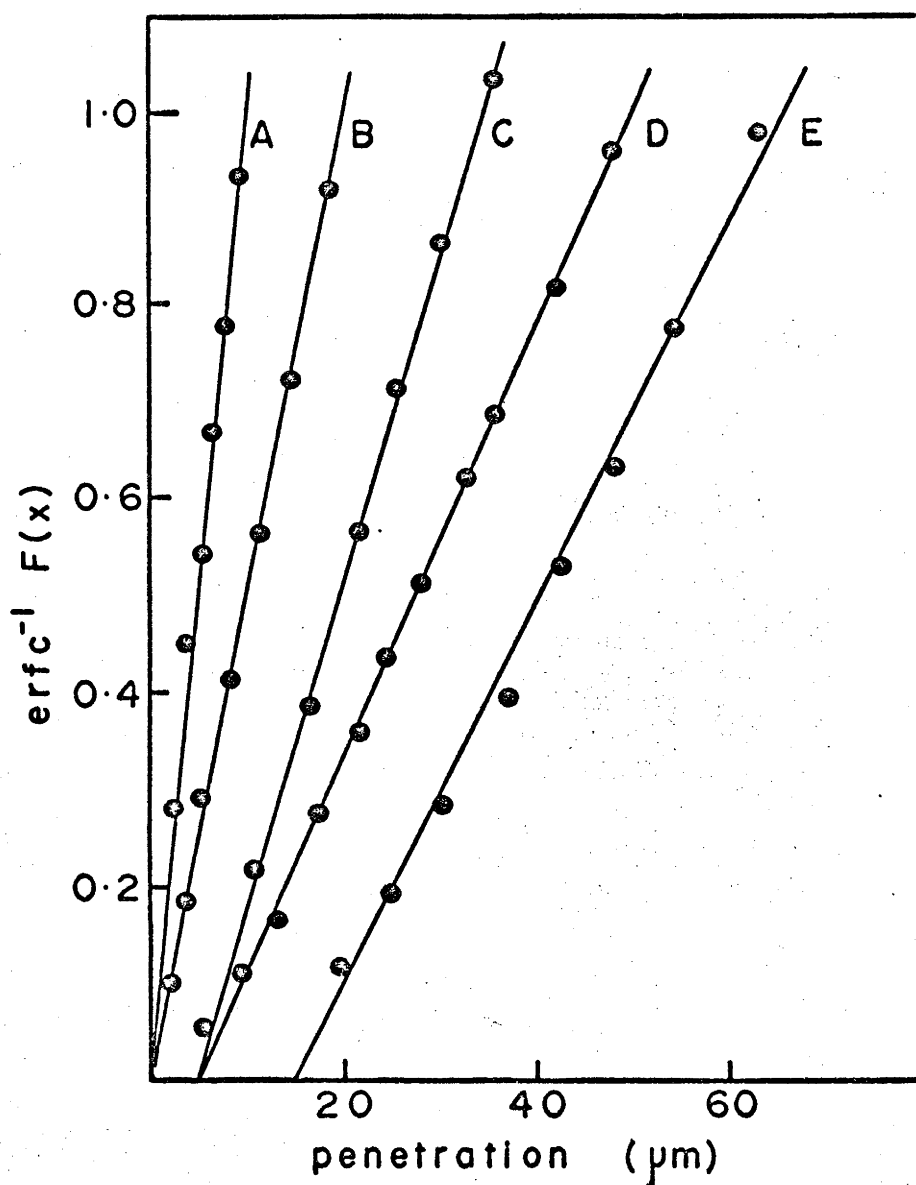


Figure 5.1. Penetration of Mg-28 into single crystal MgO for various annealing conditions.

A - 1482 °C, 2h, diluted tracer; B - 1634 °C, 2h, diluted tracer;
 C - 2084 °C, 585s, as-received tracer; D - 1650 °C, 2h, as-received tracer;
 E - 2311 °C, 585s, as-received tracer.

lines. The slight curvature in some very high temperature results was likely to have been caused by evaporation or other surface effect (see for example line 'E' in figure 5.1). Diffusion coefficients evaluated from ART experiments and DT experiments are given in tables 5.1, 5.2 and 5.3, together with details of the times and temperatures of annealings. The first results obtained [Harding, Price and Mortlock, 1971] suggested that there was a difference in purity between Ventron crystals and the Monocrystals material. However, later work showed that this was not so, and the difference in diffusion coefficients, which could not be reproduced, was attributed to a purer-than-usual batch of tracer. No distinction will be made, therefore, between samples from the different suppliers. A complete Arrhenius plot is shown in figure 5.2.

We consider first the DT results. A straight line drawn through the data for the entire temperature range leads to the following least squares equation for D,

$$D = \left(\begin{matrix} 8.59 & + 3.54 \\ & - 2.51 \end{matrix} \right) \times 10^{-4} \exp[-(2.57 \pm 0.06) \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1}. \quad (5.1)$$

It is interesting to compare this equation with that obtained by Wuensch, Steele and Vasilos [1971], namely

$$D = \left(\begin{matrix} 4.19 & + 2.45 \\ & - 1.55 \end{matrix} \right) \times 10^{-4} \exp[-(2.76 \pm 0.08) \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1}. \quad (5.2)$$

This equation describes the data shown in figure 5.3, which were obtained by a mass-spectrometric method using the stable isotope, Mg-26, as a tracer. Further discussion of these results will be given in the next chapter.

Turning to the ART results, it is apparent that these are not easily described by a single Arrhenius equation. Between 1130 °C and 1450 °C the data can be represented by

Table 5.1. Cation self-diffusion coefficients from experiments using 'as-received' tracer containing Al^{3+} , (air annealing)

T ($^{\circ}\text{C}$)	t (h)	D ($\text{cm}^2 \text{s}^{-1}$)
1132	93	1.47×10^{-12}
1134	90	1.25×10^{-12}
1206	16	6.44×10^{-12}
1209	96	4.31×10^{-12}
1241	23	7.85×10^{-12}
1280	16	1.77×10^{-11}
1282	17.3	2.18×10^{-11}
1304	61	3.04×10^{-11}
1329	16	3.60×10^{-11}
1354	4	4.85×10^{-11}
1405	12	7.29×10^{-11}
1450	5	2.33×10^{-11}
1455	2	1.99×10^{-10}
1500	1.7	2.66×10^{-10}
1557	3.3	3.95×10^{-10}
1597	4	4.65×10^{-10}
1650	2	6.43×10^{-10}
1662	2	8.34×10^{-10}
1687	1	9.05×10^{-10}
1700	2	7.27×10^{-10}
1742	1	1.08×10^{-9}
1752	1	8.58×10^{-10}

Table 5.2. Cation self-diffusion coefficients from experiments using 'as-received' tracer containing Al^{3+} , (argon annealing)

T ($^{\circ}\text{C}$)	t (s)	D ($\text{cm}^2 \text{s}^{-1}$)
1840	1170	1.58×10^{-9}
1897	885	1.87×10^{-9}
1941	900	2.71×10^{-9}
1997	885	3.12×10^{-9}
2052	870	3.91×10^{-9}
2084	585	3.65×10^{-9}
2154	900	4.99×10^{-9}
2174	580	5.08×10^{-9}
2214	870	8.03×10^{-9}
2275	580	8.65×10^{-9}
2311	585	1.34×10^{-8}
2356	890	1.50×10^{-8}

$$D = \left(\begin{matrix} 0.54 & + 0.64 \\ & - 0.29 \end{matrix} \right) \exp[-(3.2 \pm 0.1) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (5.3)$$

This region of the Arrhenius plot will be called region IV for reasons that will be explained later.

Above 1450°C , a lower activation energy appears to operate and a least squares treatment of the data up to 1900°C gives $\epsilon = (1.60 \pm 0.08) \text{ eV}$. However, towards the highest temperatures, the Arrhenius plot shows an upturn and the measured total diffusion coefficient, D_t , may well contain a contribution from intrinsic thermally produced vacancies. Assuming that purely intrinsic diffusion coefficients, D_s , are available, purely extrinsic coefficients, D_e , can be

Table 5.3. Cation self-diffusion coefficients from experiments using diluted tracer (20 X)

T (°C)	t (h or s)	D (cm ² s ⁻¹)	Atmos.
1265	31 h	3.19×10^{-12}	Air
1265	31 "	3.36×10^{-12}	"
1397	11 "	1.58×10^{-11}	"
1397	11 "	1.24×10^{-11}	"
1482	2 "	4.76×10^{-11}	"
1482	2 "	3.88×10^{-11}	"
† 1511	8 "	5.05×10^{-11}	"
1547	3 "	8.18×10^{-11}	"
1547	3 "	9.92×10^{-11}	"
† 1581	3 "	8.57×10^{-11}	"
1605	1 "	1.57×10^{-10}	"
1634	2 "	1.43×10^{-10}	"
1687	1 "	1.87×10^{-10}	"
1687	1 "	2.12×10^{-10}	"
1845	1770 s	4.70×10^{-10}	argon
1845	1770 "	4.99×10^{-10}	"
1905	1785 "	8.46×10^{-10}	"
1905	1785 "	5.94×10^{-10}	"
1969	880 "	9.74×10^{-10}	"
2019	880 "	2.12×10^{-9}	"
2028	1780 "	2.33×10^{-9}	"
2085	880 "	2.84×10^{-9}	"
2108	880 "	3.93×10^{-9}	"
2213	590 "	6.65×10^{-9}	"
2342	615 "	1.53×10^{-8}	"

† - tracer diluted only 10 X

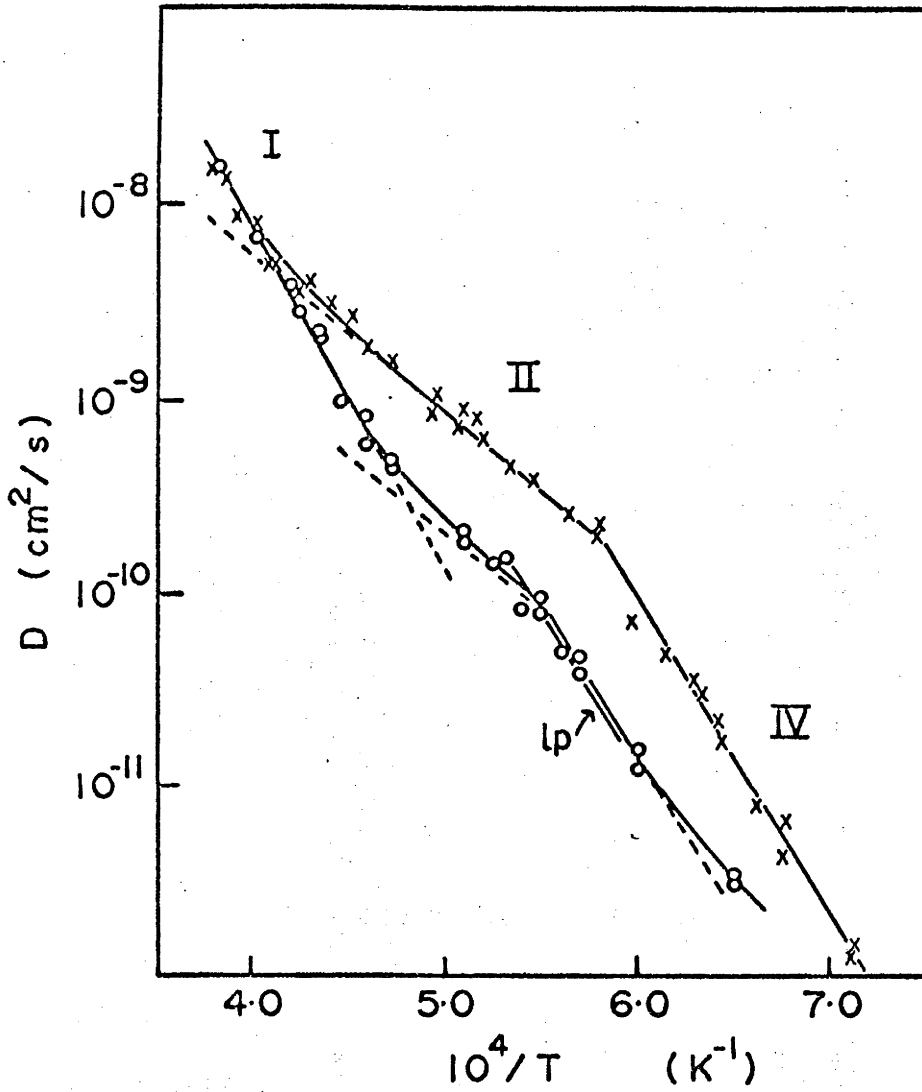


Figure 5.2. Arrhenius plot for cation self-diffusion in MgO single crystals.

- x-x- as-received tracer (ART)
- o-o- diluted (20 X) tracer (DT)
- lp Lindner and Parfitt [1957].

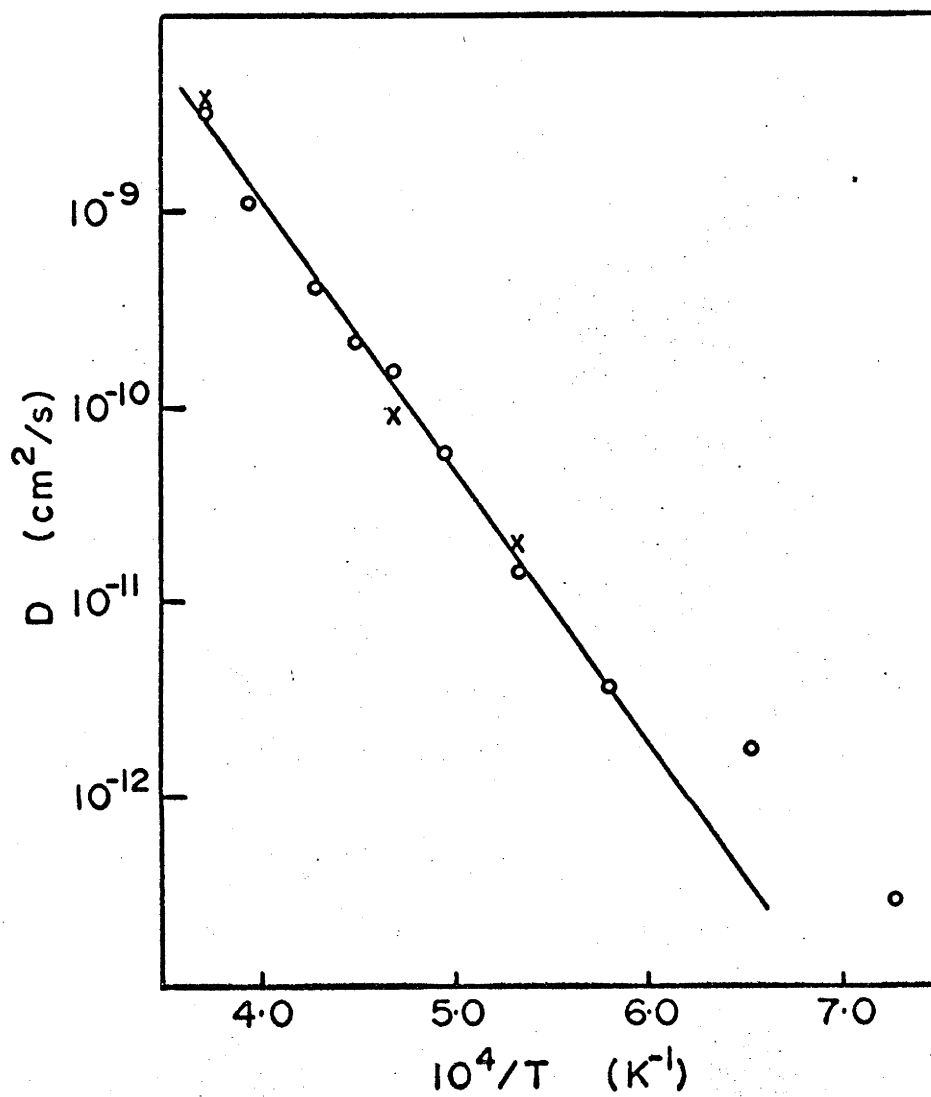


Figure 5.3. Arrhenius plot for cation self-diffusion in MgO single crystals [after Wuensch et al., 1972].

- x - W. and C. Spicer MgO.
- o - Norton Co. MgO.

calculated using equations (3.7) and (3.10) with c_i replaced by n_i , the vacancy concentration arising from impurities. We have

$$n_i = n_c - \frac{n_o^2}{n_c} \quad (5.4)$$

where n_c and n_o have been defined previously. Taking diffusion coefficients to be proportional to the corresponding cation vacancy concentrations, we can write

$$D_e = D_t - \frac{D_t^2}{D_t} \quad (5.5)$$

It should now be noted that the ART coefficients and the DT coefficients coincide at temperatures above 2100 °C and in view of the differing purities of the samples concerned, one is led to suggest that, at these temperatures, diffusion is indeed intrinsic. Re-considering the DT results, it is found that coefficients at 1900 °C and above are given by

$$D = \left(\begin{matrix} 7.43 & + & 12.17 \\ & - & 4.61 \end{matrix} \right) \times 10^{-2} \exp[-(3.46 \pm 0.19) \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1} \quad (5.6)$$

Inclusion of points at lower temperatures gave lower activation energies. It should be noted that the difference in activation energies in equations (5.6) and (5.1) is well outside the standard error limits. Assuming that equation (5.6) describes purely intrinsic diffusion, we can now use equation (5.5) to calculate the equation for purely extrinsic diffusion. The result is

$$D = 7.48 \times 10^{-6} \exp[-1.56 \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1} \quad (5.7)$$

This line is shown broken in figure 5.2. It is reasonable, because of the very small difference between equation (5.7) and the least squares line for points between 1450 °C and 1900 °C, to assume similar error limits and write the extrinsic activation energy as $(1.56 \pm 0.08) \text{ eV}$.

In future discussion, the intrinsic and extrinsic regions of diffusion will be referred to as regions I and II respectively.

Since the ART data can be divided into a lower region IV, and an extrinsic region II with an increasing contribution from intrinsic diffusion at very high temperatures, it is reasonable to look for a similar structure in the Arrhenius plot for the DT results. From 1800-1540 °C, the data points do indeed show some curvature. If equation (5.6) is used to obtain purely intrinsic coefficients in this range, equation (5.5) leads to extrinsic coefficients given by

$$D = 1.66 \times 10^{-6} \exp[-1.55 \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (5.8)$$

The activation energy here agrees well with that obtained over the much wider temperature range covered by the ART experiments for region II.

Below 1540 °C, a downturn in the Arrhenius plot occurs and there is good agreement between this data and those published by Lindner and Parfitt [1957], indicated in figure 5.2 by the line 'lp'. Indeed, the existence of region IV diffusion accounts for the high activation energy obtained in the early work. The DT coefficients for 1265 °C are somewhat high, this small enhancement being found also for Ni^{2+} diffusion in MgO. This is in accord with a brief reference by Lindner and Parfitt to a lower activation energy process below 1400 °C. Diffusion coefficients became too small to measure below 1265 °C in the time available and this, combined with the likely interference from short-circuit effects, made it difficult to evaluate an activation energy for region IV in this case.

It seems unlikely that atmosphere has any effect on D in the intrinsic region (I), since if such an effect existed, it would have resulted in a curved Arrhenius plot, the oxygen partial pressure (p_{O_2}) in the magnesia containers being uncontrolled. With the equipment available, it was not possible to perform annealings in air above

1750 °C. In the Ni and Ba diffusion studies, no p_{O_2} dependence of D was found below 1700 °C, although such a dependence of conductivity has been found [Mitoff, 1959, 1962; Osburn and Vest, 1971] in this temperature range. This problem will be discussed further in chapter 6.

Two experiments, at 1511 °C and 1581 °C, using tracer diluted only 10 times, gave results that were not significantly different from those to be expected from samples in which a dilution factor of 20 was used. Furthermore, the 'knee' temperature between regions I and II (about 1800 °C) agrees with the results for Ni and Ba impurity diffusion in MgO crystals from the same supplier. This confirms that the average Al^{3+} content introduced via the tracer in the DT experiments was less than the grown-in impurity content of the MgO crystals.

5.2. Nickel diffusion in MgO

The Gruzin method (equation (4.10)) was used to determine diffusion coefficients for nickel in MgO, although the correction is small because μ is large (5000 cm^{-1}). At temperatures below 1800 °C in air, the concentration function, $c(x)$, is given by equation (2.5) because the Ni^{2+} dissolves rapidly in the MgO lattice. Above 1800 °C in argon, the Ni^{2+} was much less soluble and a thin surface excess was present throughout the short annealings. Therefore, equation (2.6) was used for these conditions. The penetration of Ni^{2+} into MgO is shown in figures 5.4 and 5.5 for the very high temperature runs in argon and the lower temperature air runs respectively. Reasons for the failure of these graphs to pass through the origin have been discussed already. The Arrhenius plot for nickel diffusion in MgO is shown in figure 5.6. Table 5.4 gives details of the diffusion coefficients measured and the relevant annealing times and temperatures.

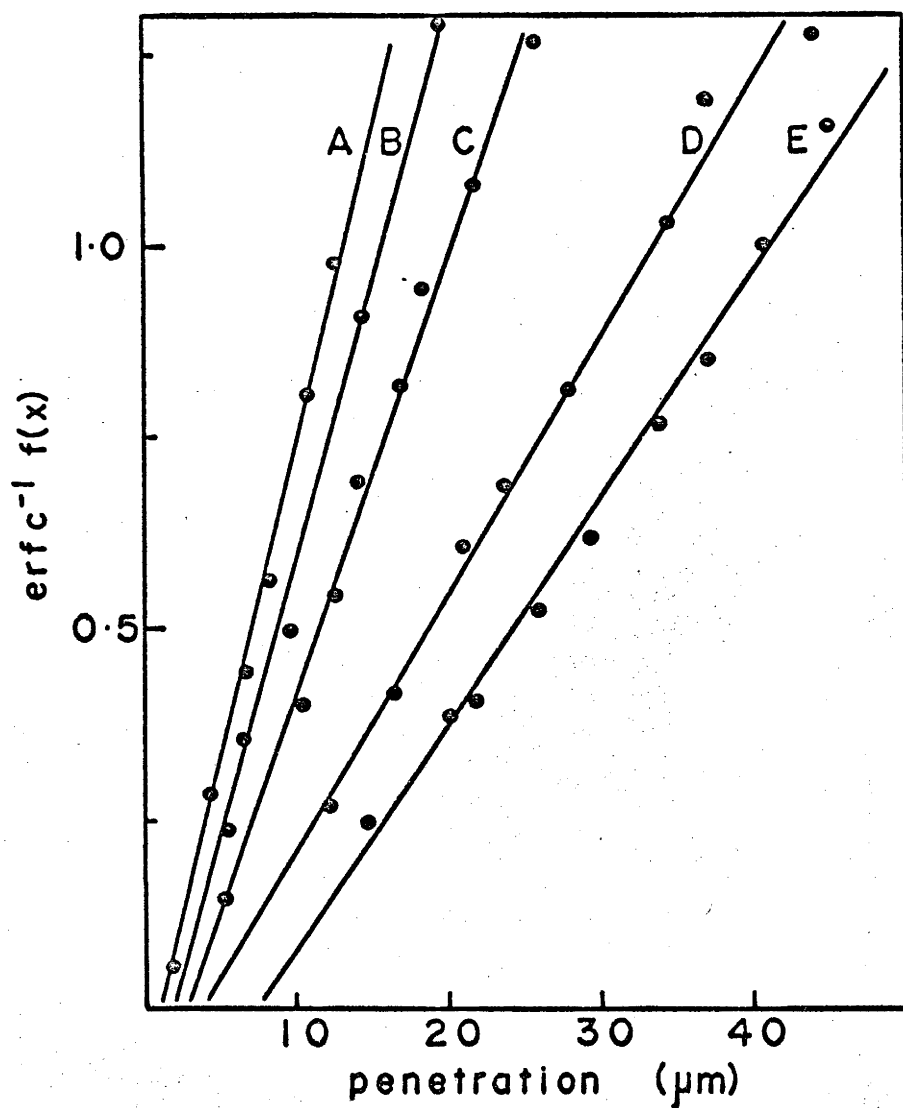


Figure 5.4. Penetration of Ni-63 into single crystal MgO for various annealing conditions (high temperature, argon atmosphere)..

A - 1803 °C, 14m, Al^{3+} added; B - 1800 °C, 1h; C - 1957 °C, 29m;
D - 2059 °C, 29m; E - 2260 °C, 19.5m.

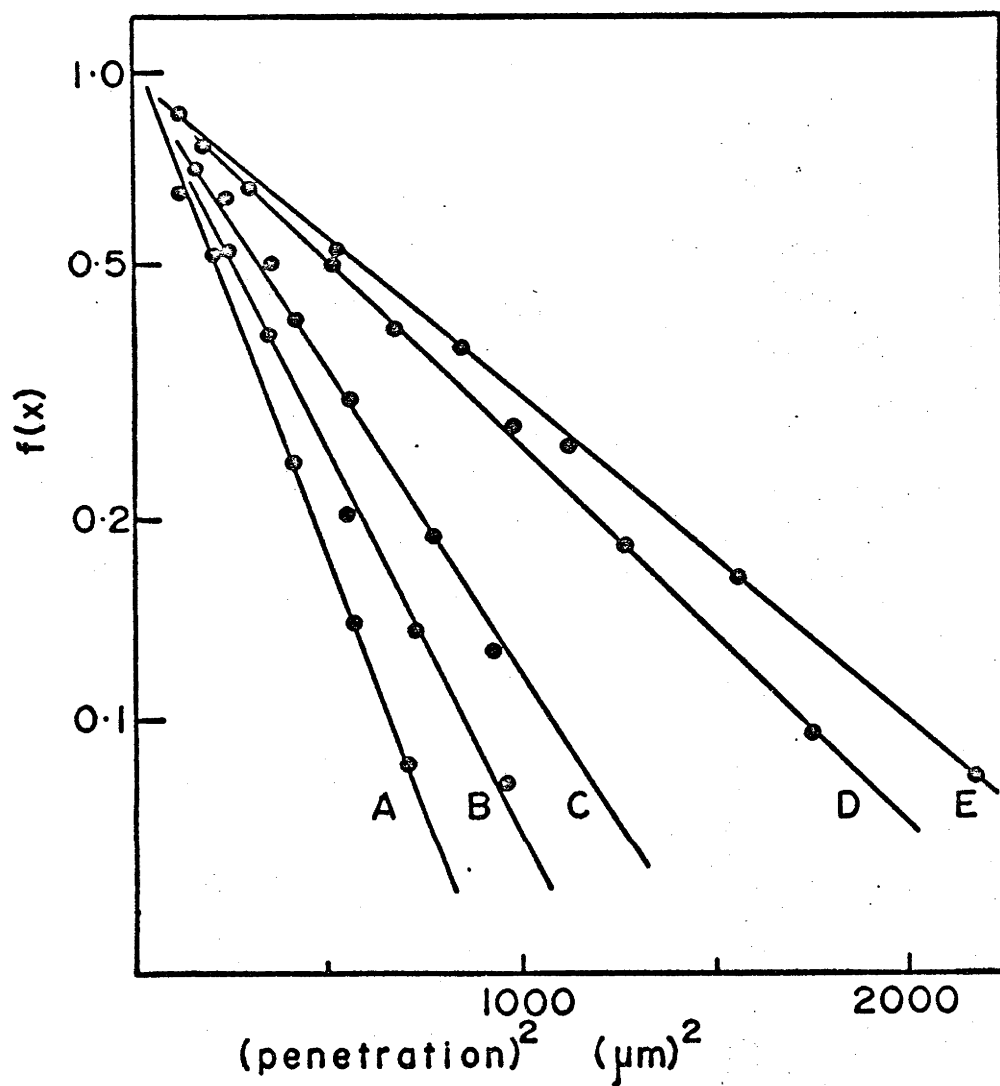


Figure 5.5. Penetration of Ni-63 into single crystal MgO for various annealing conditions ($< 1750^\circ\text{C}$, air atmosphere).

A - 1198°C , 187h; B - 1512°C , 2h, Al^{3+} added; C - 1669°C , 4h;
D - 1511°C , 22h; E - 1315°C , 140h.

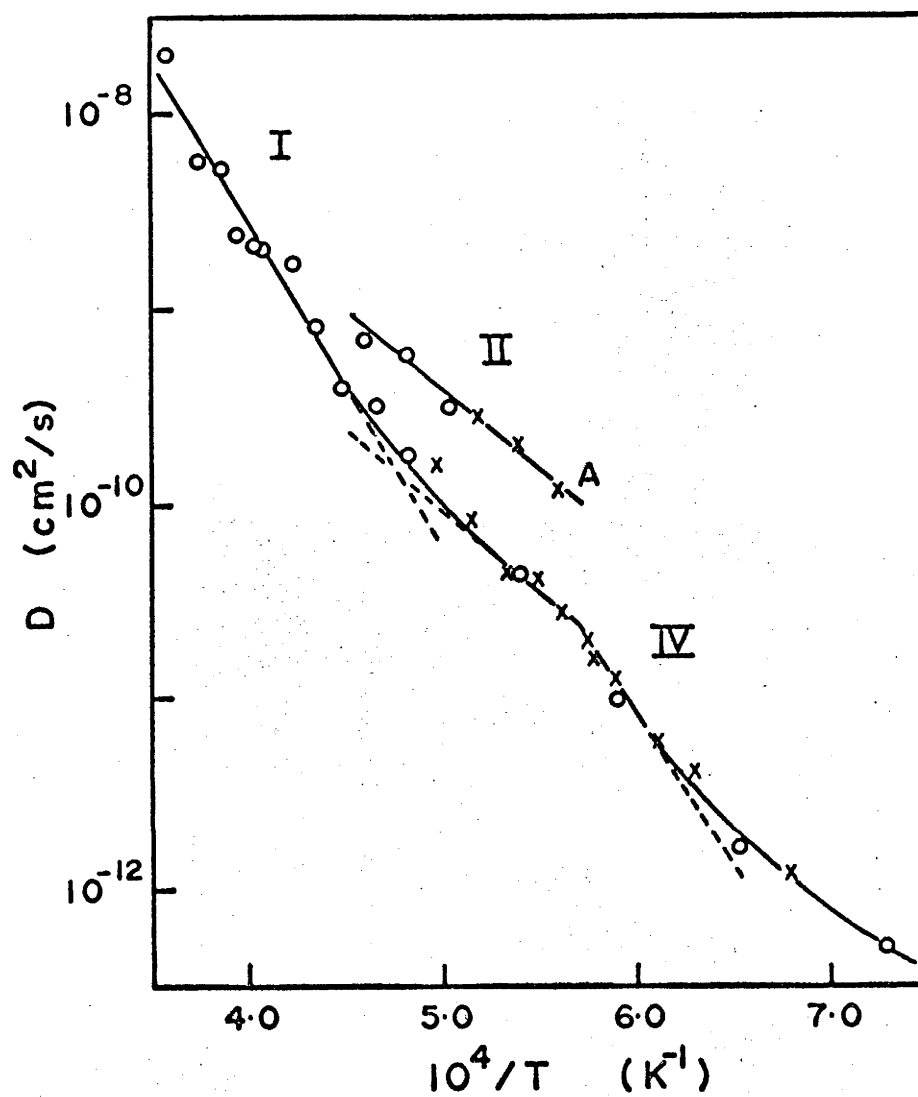


Figure 5.6. Arrhenius plot for Ni diffusion in single crystal MgO.

x - air annealing; o - argon annealing; line 'A' - Al^{3+} added to tracer.

Table 5.4. Diffusion coefficients for Ni^{2+} in single crystal MgO

T ($^{\circ}\text{C}$)	t (h or s)	D ($\text{cm}^2 \text{s}^{-1}$)	Atmos.
1100	764 h	5.10×10^{-13}	argon
1198	187 "	1.24×10^{-12}	air
1258	912 "	1.67×10^{-12}	argon
1315	140 "	4.15×10^{-12}	air
1360	94 "	6.12×10^{-12}	"
1421	49 "	1.00×10^{-11}	argon
1421	134 "	1.27×10^{-11}	air
1422	52 "	9.88×10^{-12}	argon
1458	30 "	1.58×10^{-11}	air
1465	27 "	1.99×10^{-11}	"
1511	22.3 h	2.84×10^{-11}	"
1544	20 h	4.25×10^{-11}	"
1579	20 "	4.51×10^{-11}	argon
1604	8 "	4.41×10^{-11}	air
1669	4 "	8.50×10^{-11}	"
1740	3900 s	1.61×10^{-10}	"
1800	3600 "	1.76×10^{-10}	argon
1870	1770 "	3.16×10^{-10}	"
1957	1740 "	3.87×10^{-10}	"
2026	1740 "	8.20×10^{-10}	"
2059	1740 "	1.69×10^{-9}	"
2192	1140 "	2.07×10^{-9}	"
2207	900 "	2.11×10^{-9}	"
2260	1170 "	2.41×10^{-9}	"
2311	900 "	5.32×10^{-9}	"
2392	1110 "	5.75×10^{-9}	"
2518	1500 "	2.06×10^{-8}	"

Since we are dealing here with crystals from the same source as those used in the self-diffusion studies, it is not unreasonable to look for the same structure in the Arrhenius plot. Indeed, it is possible to divide the plot for Ni^{2+} diffusion into three regions, and apart from the somewhat lower diffusion coefficients, figure 5.6 is very similar to figure 5.2. A least squares treatment of the data over 1900°C leads to the following equation for intrinsic (region I) diffusion:-

$$D = \left(\begin{matrix} 0.014 & + 0.048 \\ & - 0.011 \end{matrix} \right) \exp[-(3.3 \pm 0.3) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (5.9)$$

Region II (extrinsic) diffusion covers only a narrow temperature range and results were treated in a similar manner to the corresponding self-diffusion data, using equations (5.5) and (5.9). It was found that region II diffusion can be represented by

$$D = 1.3 \times 10^{-6} \exp[-1.6 \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (5.10)$$

Below about 1500°C , there is a downturn in the Arrhenius plot (region IV). Again, as in self-diffusion, there is a slight enhancement, by a short-circuit mechanism, of coefficients at the lowest temperatures and it is not possible to give an accurate value of δ in this temperature range. However, a tangent drawn at the point where the downturn occurs yields an activation energy of 3.2 eV and a D_0 of $0.028 \text{ cm}^2 \text{ s}^{-1}$. This is shown as a broken line in figure 5.6.

It is possible to ignore the structure of the Arrhenius plot and draw a straight line through all data points. This line is given by

$$D = \left(\begin{matrix} 1.86 & + 0.71 \\ & - 0.51 \end{matrix} \right) \times 10^{-4} \exp[-(2.41 \pm 0.05) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (5.11)$$

which may be compared with the data obtained by Wuensch and Vasilos

[1971] shown in figure 5.7. The equation for D published by these authors is

$$D = 1.80 \times 10^{-5} \exp[-2.10 \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} \quad (5.12)$$

for a similar temperature range to that covered by the experiments reported here. To assist in deciding between these alternative treatments of the data, several experiments were done in which equal amounts of Al^{3+} ($2 \mu\text{g}$) were added to the Ni-63 tracer solution deposited on each of the MgO samples. This reproduced the conditions of the self-diffusion experiments using as-received Mg-28. The diffusion coefficients obtained are given in table 5.5 and are plotted in figure 5.6. The line, 'A', drawn through this data gives an activation energy of 1.6 eV in agreement with equation (5.10), rather than the alternative (2.41 eV). The coefficients show a four times enhancement (cf. self-diffusion) over those obtained with as-received Ni-63 and the extrinsic region II is extended to cover a wider temperature range.

Table 5.5. Diffusion coefficients for Ni^{2+} in single crystal MgO from experiments in which Al^{3+} was added to the tracer solution

$T (^{\circ}\text{C})$	$t \text{ (s)}$	$D \text{ (cm}^2 \text{ s}^{-1}\text{)}$	Atmos.
1512	7200	1.18×10^{-10}	air
1579	3600	2.02×10^{-10}	"
1649	3600	2.73×10^{-10}	"
1714	1740	3.16×10^{-10}	argon
1803	840	5.90×10^{-10}	"
1900	840	7.00×10^{-10}	"

There appears to be no atmosphere effect in region I for reasons already mentioned in section 5.1. Several experiments performed

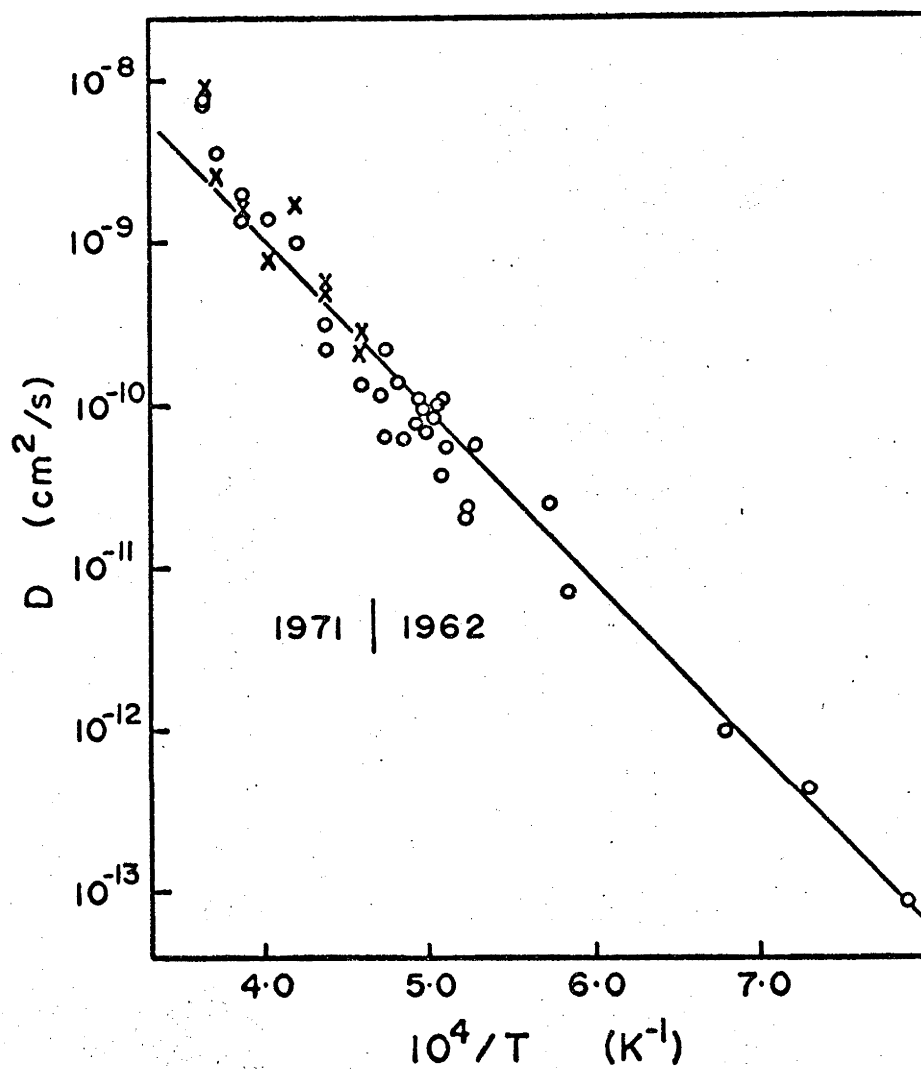


Figure 5.7. Arrhenius plot for Ni diffusion in single crystal MgO [after Wuensch and Vasilos, 1971].

- x - W. and C. Spicer MgO.
- o - Norton Co. MgO.

in argon in the temperature range below 1750 °C gave results in agreement with those from air annealings suggesting that atmosphere effects on Ni^{2+} diffusion in MgO are negligible.

5.3. Barium diffusion in MgO

Barium diffusion in MgO has been studied previously and some results for the temperature range 1000-1700 °C have been published [Harding, 1967a]. It was found that profiles consisted, in general, of three parts. That nearest the surface (part A) was considered to be due to lattice diffusion. The second and third parts (parts B and C) lying deeper in the crystal can be explained as being caused by short-circuit paths [Harding, 1971]. The method of evaluating diffusion coefficients from the multi-component profiles was described in the earlier paper.

Barium was found to be very insoluble in MgO and hence equation (4.7) was used in the analysis of the experimental penetration profiles. Graphs of $\text{ierfc}^{-1} F(x)/1.772$ are plotted against x in figure 5.8 for several samples. Table 5.6 lists measured diffusion coefficients, together with annealing times and temperatures. Some experiments below 1700 °C were performed in argon for comparison with air annealings, but, again, no atmosphere effect was detected. The Arrhenius plot for points down to 1228 °C is shown in figure 5.9. A line drawn through results obtained in the very high temperature region was found to be displaced downwards relative to the earlier lower temperature data. Therefore, taking all points above 1900 °C as representing region I diffusion, a least squares treatment gives

$$D = \left(\begin{matrix} 0.028 & + 0.132 \\ & - 0.023 \end{matrix} \right) \exp[-(3.5 \pm 0.3) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (5.13)$$

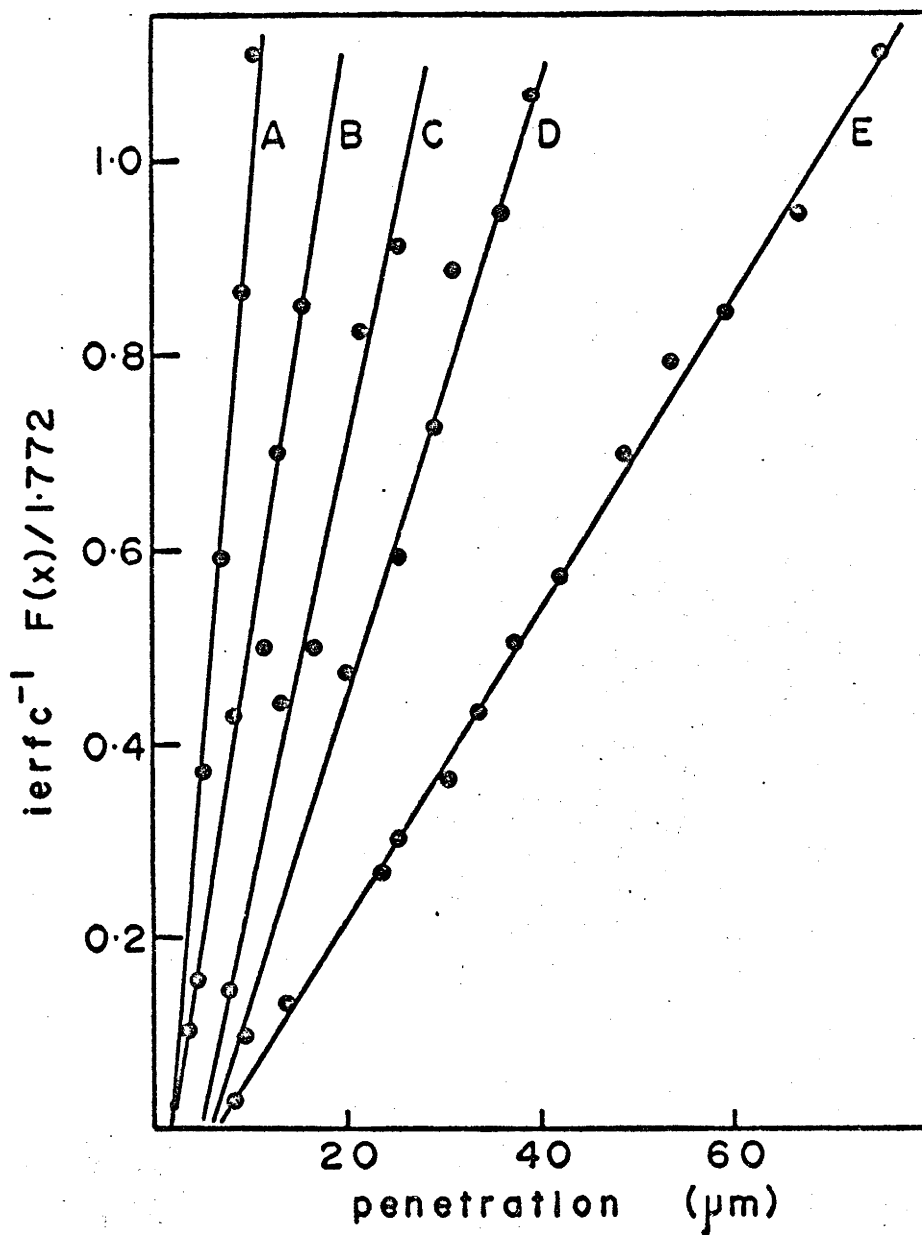


Figure 5.8. Penetration of Ba-133 into single crystal MgO for various annealing conditions.

A - 1120 °C, 840h, air; B - 1363 °C, 96h, air; C - 1611 °C, 9h, argon; D - 2064 °C, 39m, argon; E - 2233 °C, 29m, argon.

Table 5.6. Diffusion coefficients for Ba^{2+} in MgO single crystals (Monocrystals material, except where marked V)

T ($^{\circ}\text{C}$)	t (h or s)	D ($\text{cm}^2 \text{s}^{-1}$)	Atmos.
1008	1319 h	3.56×10^{-15}	air
1008	1319 "	3.62×10^{-15}	"
1120	840 "	7.24×10^{-14}	"
1124	1075 "	6.51×10^{-14}	"
1228	604 "	2.70×10^{-13}	"
1228	604	2.64×10^{-13}	"
1277	62.5 h	7.20×10^{-13}	"
1361	24 h	3.00×10^{-12}	"
1363	96 "	2.12×10^{-12}	"
1422	37 "	8.87×10^{-12}	argon
1422	37 "	5.49×10^{-12}	"
1507	5 "	1.93×10^{-11}	air
1507	5 "	2.39×10^{-11}	"
1546	9 "	3.20×10^{-11}	argon
1594	14.5 h	2.90×10^{-11}	air
1607	23 h	5.41×10^{-11}	"
1611	9.2 h	2.99×10^{-11}	argon
1651	6 h	3.87×10^{-11}	air
1651	6 "	4.70×10^{-11}	"
1689	5.5 h	4.95×10^{-11}	argon
1714	7 h	8.20×10^{-11}	air
1793	2 "	1.15×10^{-10}	argon
1852	1770 s	1.89×10^{-10}	" V
1900	1770 "	2.15×10^{-10}	" V
1937	3540 "	5.60×10^{-10}	"
2000	1770 "	4.17×10^{-10}	" V
2064	2340 "	1.18×10^{-9}	"
2150	14,400 "	1.34×10^{-9}	"
2233	1740 "	5.38×10^{-9}	"
2418	570 "	1.03×10^{-8}	"
2445	1590 "	7.89×10^{-9}	"

V - Ventron MgO

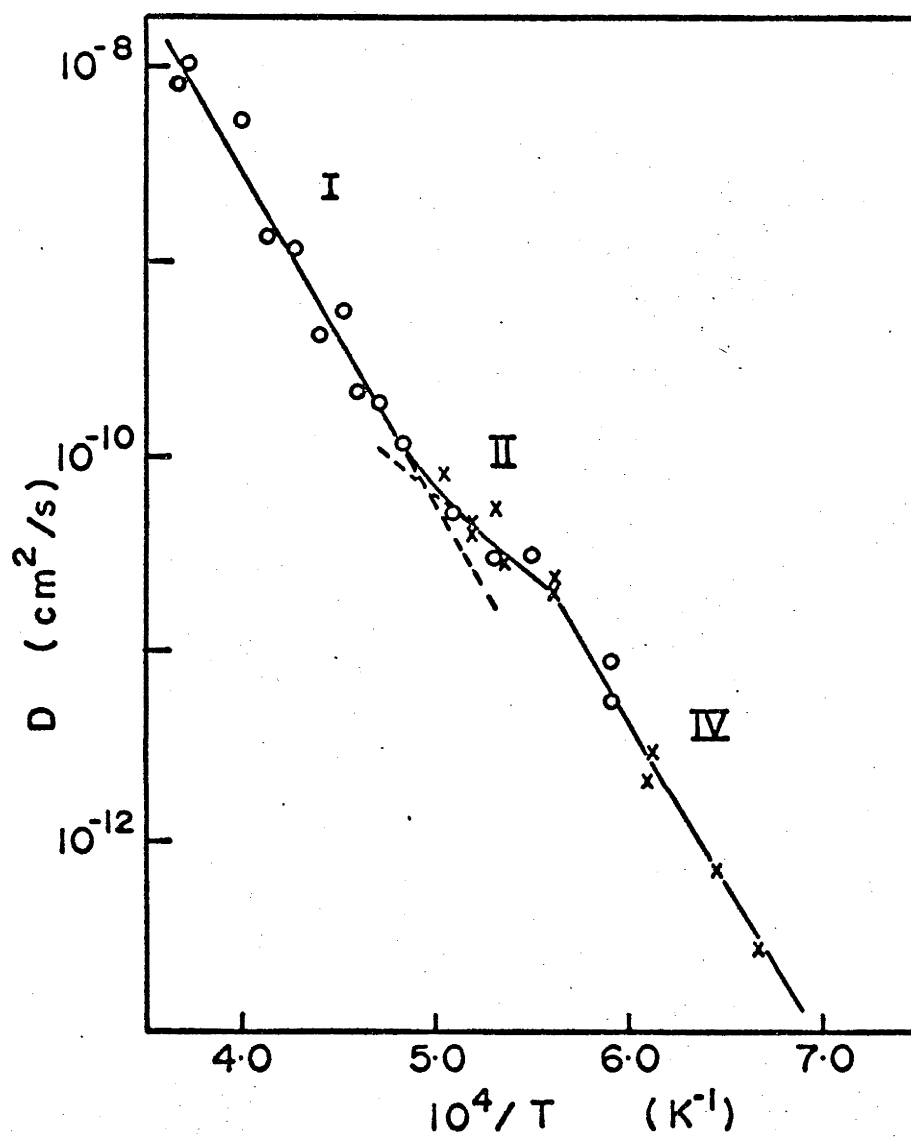


Figure 5.9. Arrhenius plot for Ba diffusion in MgO single crystals.

x - air annealings; o - argon annealing.

In the case of Ba^{2+} , short circuit contributions to diffusion can be separated from lattice diffusion and it is possible to obtain lattice diffusion coefficients down to the lowest temperatures (1000 °C). The differences between the mechanisms of short-circuit diffusion of Ba^{2+} and Ni^{2+} in MgO will be discussed later. A least squares treatment of the data below 1500 °C leads to an Arrhenius equation for what will again be called region IV diffusion. We have

$$D = \left(\begin{matrix} 0.042 & + & 0.054 \\ & - & 0.023 \end{matrix} \right) \exp[-(3.3 \pm 0.1) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} \quad (5.14)$$

in agreement with the equation previously published [Harding, 1967a].

Between the two clearly defined lines (equations (5.13) and (5.14)) the data points are rather scattered, the situation being aggravated by the very low count rates arising from the low solubility of barium in MgO. It is therefore not possible to assign an activation energy to region II, in the way that was done for Mg^{2+} and Ni^{2+} diffusion. However, from the activation energies for region I and region IV, a value of 1.6 eV can be obtained.

Again, the alternative interpretation of the barium diffusion results is to draw a single straight line Arrhenius plot giving an activation energy of 2.9 eV for the entire temperature range (1000-2450 °C).

In order to investigate the previously mentioned parts B and C of the barium diffusion profiles, the experiments described in section 4.4.2 were performed. Six diffusion sandwiches, which had been carefully made up from pre-annealed MgO crystals; were diffusion-annealed in air for 1 hour at 1580 °C. For such a short time, the $\sqrt{Dt}$ for lattice diffusion was only about 3 μm , and in only one case was the coefficient for part A evaluated. Figure 5.10 shows a series of integrated profiles obtained by plotting the activity remaining

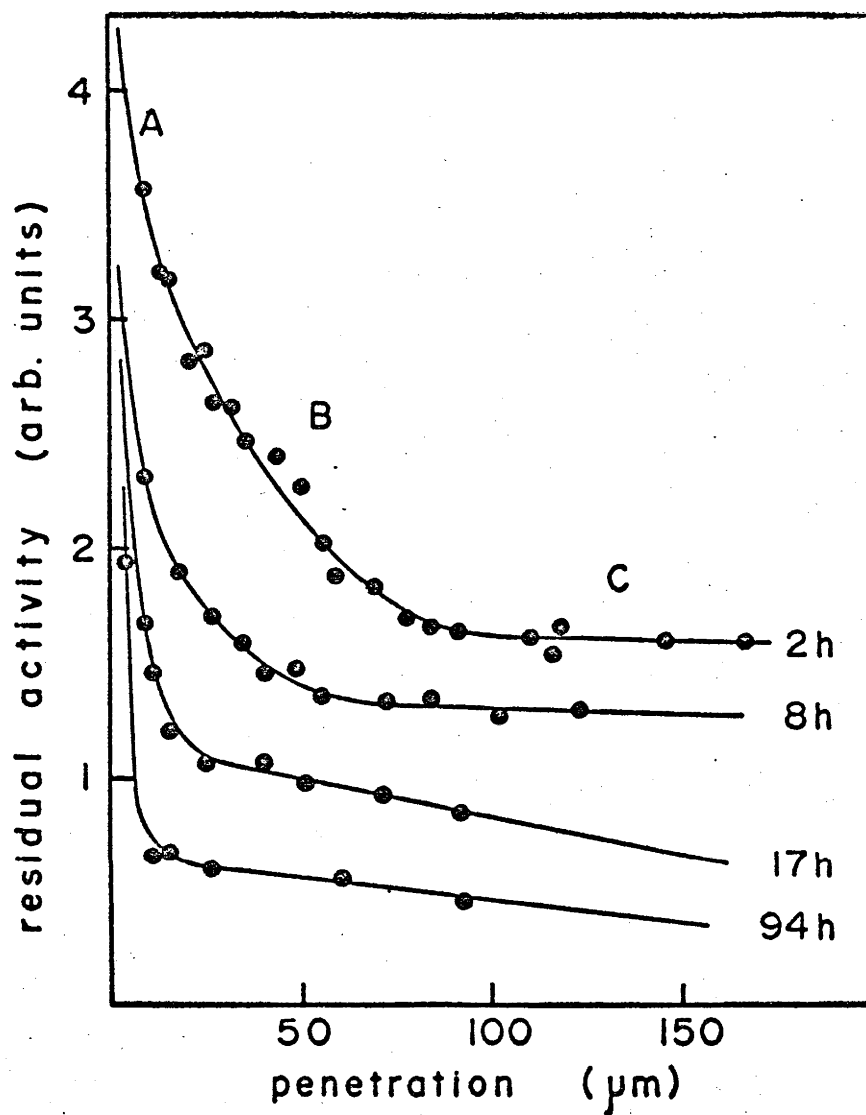


Figure 5.10. Integrated penetration profiles for Ba-133 into MgO single crystals after diffusion annealing for 1h at 1580 °C, for various pre-annealing times.

A - lattice diffusion; B and C - short-circuit diffusion.

(arbitrary units) after material had been removed to a depth 'x' against penetration distance (μm) for samples pre-annealed for 2, 8, 17 and 94 hours. The three component parts (A, B and C) are clearly present in the profile for the sample pre-annealed for only 2 hours. Part B for each profile yielded the diffusion coefficients, D , plotted against pre-annealing time in figure 5.11 and listed in table 5.7. Although not strictly correct, lattice diffusion mathematics were applied here in the manner described earlier [Harding, 1967a, 1967b]

Table 5.7. Diffusion coefficients for Ba^{2+} in MgO obtained from part B of the diffusion profiles after 1 h annealing at 1580°C , as a function of pre-annealing time

Pre-annealing time (h)	$D (\text{cm}^2 \text{s}^{-1})$
0	1.51×10^{-9}
0	1.36×10^{-9}
2	3.09×10^{-9}
2	4.03×10^{-10}
8	1.65×10^{-9}
8	1.58×10^{-10}
17	2.38×10^{-10}
17	5.60×10^{-11}
26	7.04×10^{-10}
26	2.50×10^{-11}
94	2.82×10^{-11}
94	3.74×10^{-10}

so that results could be compared with those obtained for the 'second region' in the previous study. The third part, C, of the profiles comprises a long tail persisting to large penetrations, even for the sample pre-annealed for the longest time. In spite of the large variations in the D 's for part B, it can be seen that they tend to approach the true volume diffusion coefficient as the pre-annealing time is increased, and there is little doubt that the defects

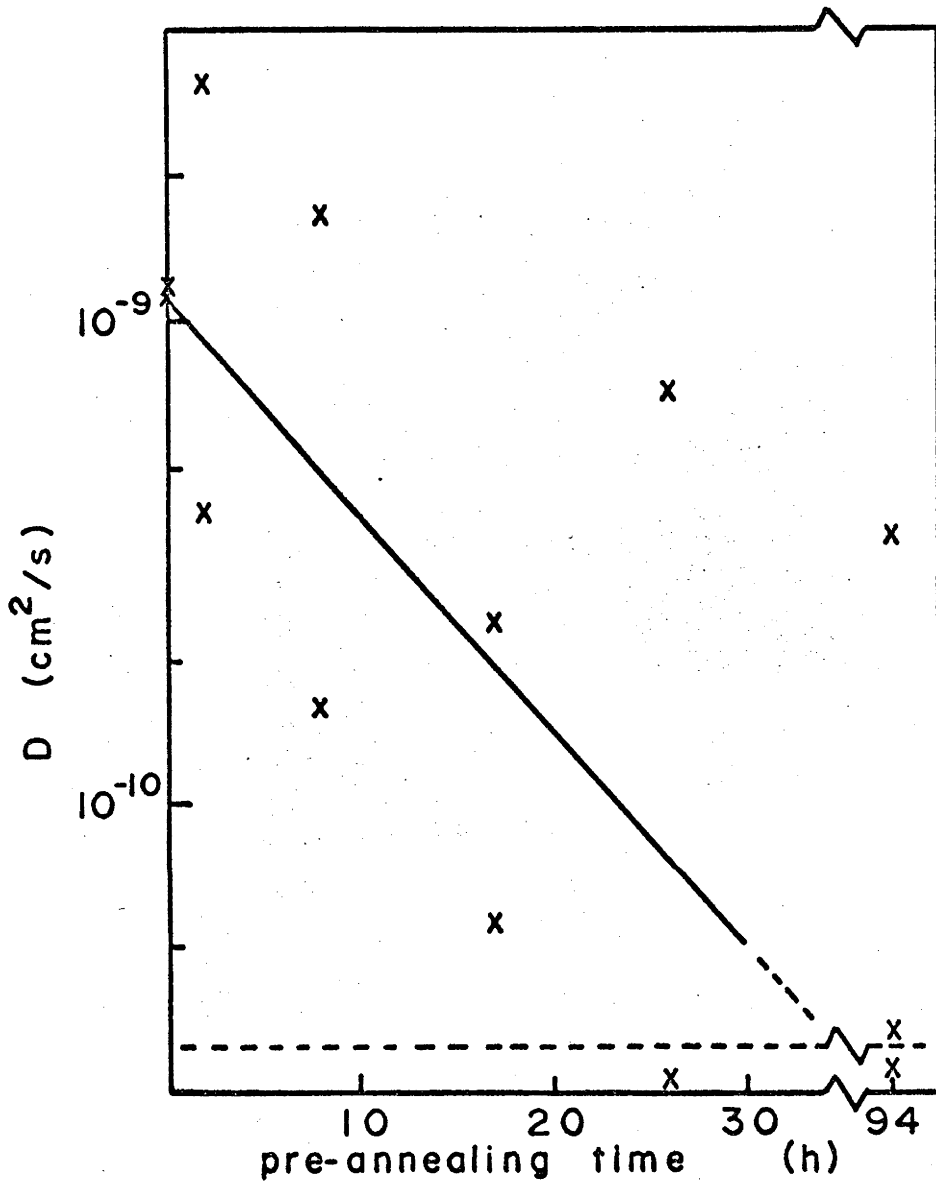


Figure 5.11. Diffusion coefficients evaluated from part B of the penetration profiles in figure 5.10 plotted against pre-annealing time. The broken line is the lattice diffusion coefficient for 1580°C .

responsible anneal out with time. Hence, the second region eventually vanishes. The scatter of points may be due to a variation in the initial concentration of defects from crystal to crystal, or to the re-introduction of defects during the preparation of the diffusion sandwiches following pre-annealing. For example, in one half of the couple pre-annealed for 94 hours, the second part (B) was missing, whereas the other half yielded a complete three-part profile.

It is evident, then, that diffusion coefficients plotted previously as 'dislocation influenced' diffusion [see figure 3, Harding, 1967a] depend not only on the time of annealing, but also on the extent of damage in any particular sample. It is therefore meaningless to calculate an activation energy for diffusion coefficients evaluated from part B of the experimental profiles in this work, and in many cases only the lattice diffusion coefficient was calculated.

5.4. Cadmium diffusion in MgO .

The diffusion of cadmium in MgO was studied over the temperature range 1770-2270 °C, using the tracer Cd-115m [Harding and Bhalla, 1971]. The Gruzin analysis was applied to a typical experimental profile and it was found that μA_n was only about 5% of $\partial A_n / \partial x_n$ (see equation (4.10)). The graphical evaluation of the sum $(\mu A_n - \partial A_n / \partial x_n)$ led to greater errors than were introduced by neglecting the absorption term completely and using the integrated equation (4.5). The straight lines obtained in plotting $\operatorname{erfc}^{-1} F(x)$ vs. x (figure 5.12) confirmed this. Diffusion coefficients obtained are listed in table 5.8 along with other experimental details, and the graph of $\log D$ against $1/T$ is shown in figure 5.13. The straight line drawn through the points can be described by the equation

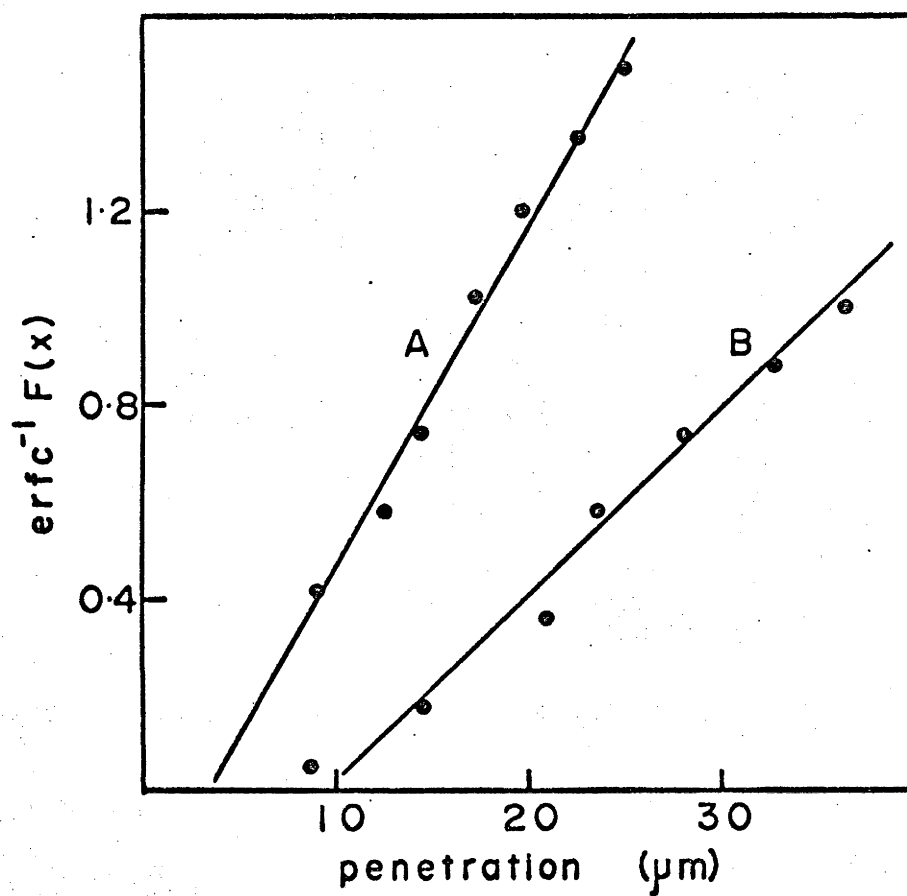


Figure 5.12. Penetration of Cd-115m into single crystal MgO.

A - 2017 °C, 20m; B - 2267 °C, 14.5m.

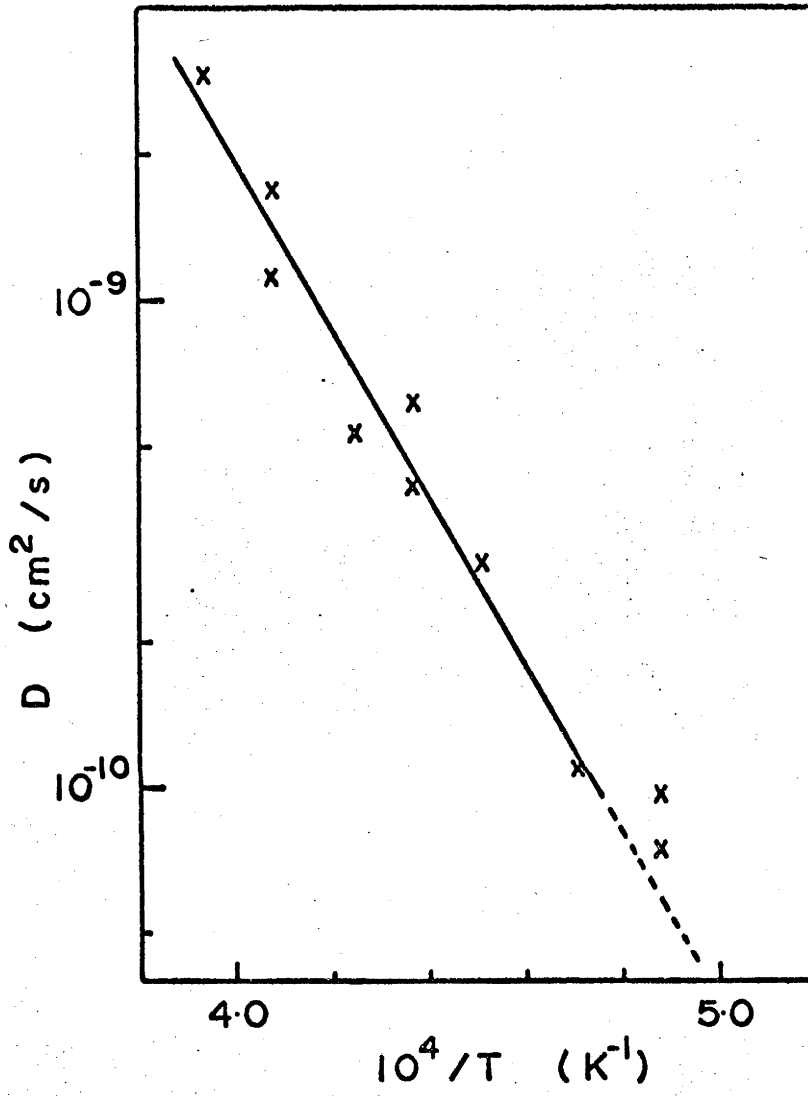


Figure 5.13. Arrhenius plot for Cd diffusion in MgO single crystals.

Table 5.8. Diffusion coefficients for Cd^{2+} in MgO single crystals (argon atmosphere)

T ($^{\circ}\text{C}$)	t (s)	D ($\text{cm}^2 \text{s}^{-1}$)
1778	3540	7.47×10^{-11}
1778	3540	9.59×10^{-11}
1849	1170	1.09×10^{-10}
1945	1770	2.91×10^{-10}
2017	1200	4.11×10^{-10}
2017	1200	6.19×10^{-10}
2080	1170	5.28×10^{-10}
2179	870	1.67×10^{-9}
2179	870	1.10×10^{-9}
2267	870	2.92×10^{-9}

$$D = \left(\begin{matrix} 0.017 + 0.060 \\ - 0.014 \end{matrix} \right) \exp[-(3.4 \pm 0.3) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} \quad (5.15)$$

where errors have again been derived from a least squares treatment of the data. In view of the likely contribution from extrinsic diffusion, the data for 1778°C were omitted from the calculation leading to equation (5.15), which is considered to relate to intrinsic diffusion.

5.5. Calcium diffusion in MgO

For comparison with Cd^{2+} which has the same ionic radius, Ca^{2+} diffusion in MgO was studied over a similar temperature range. In this case, however, absorption of the 0.26 MeV β rays in MgO was significant. The absorption curve has been given in figure 4.12 and does not deviate very far from an exponential. The value of μ was taken as 430 cm^{-1} . The Gruzin equation (4.10) was again used to analyse the raw profile data and in this case, the contributions from the two terms on the left hand side were about equal. This led to a greater scatter of points on the $\log f(x)$ vs. x^2 plots (figure 5.14) than in the other

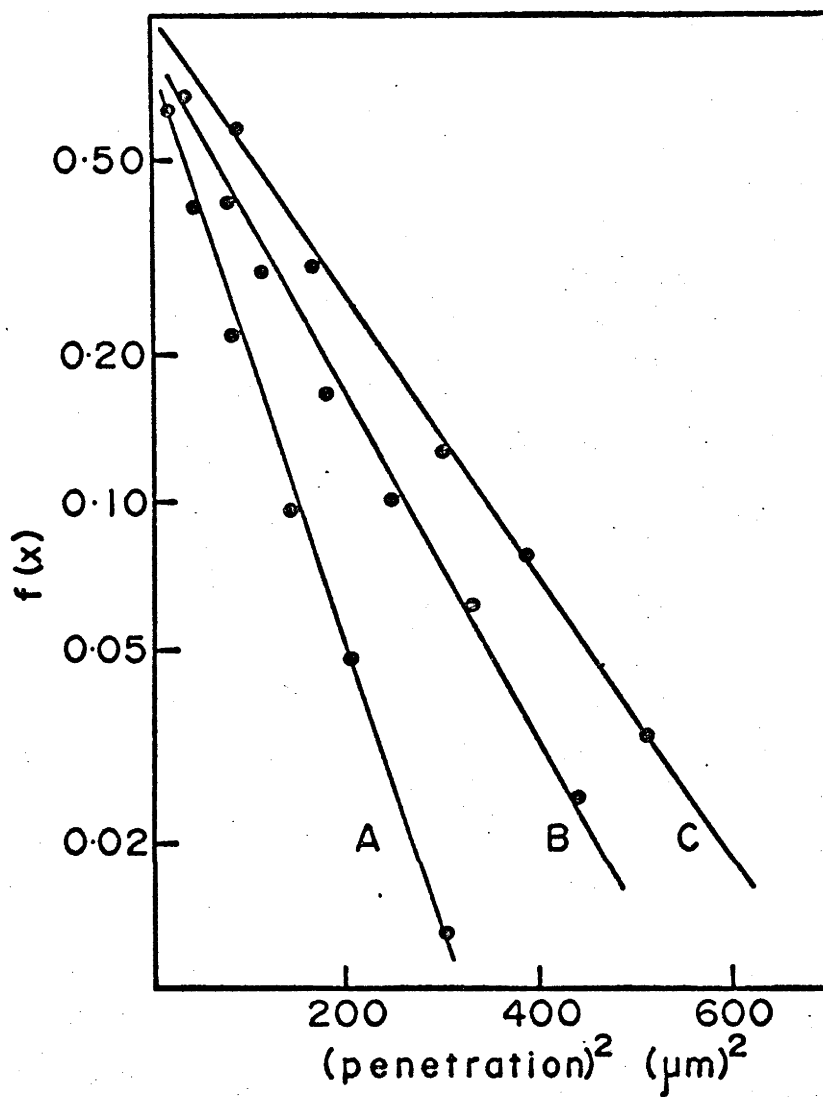


Figure 5.14. Penetration of Ca-45 into MgO single crystals.

A - 1922 °C, 29.5m; B - 1998 °C, 19.5m; C - 2080 °C, 14.5 m.

experiments. The graph of $\log D$ vs. $1/T$, for the temperature range 1850-2380 °C, is shown in figure 5.15 and table 5.9 gives the relevant details. The equation for D is

$$D = \left(3.43 + \frac{4.95}{-2.03} \right) \times 10^{-3} \exp [-(3.2 \pm 0.2) \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1} \quad (5.16)$$

and, as before, is considered to relate to region I diffusion. The activation energy is higher than both of the previously published values for diffusion at lower temperatures [Rungis and Mortlock, 1966; Wuensch and Vasilos, 1968]. A comparison of these results is shown in figure 5.16.

Table 5.9. Diffusion coefficients for Ca^{2+} in single crystal MgO (argon atmosphere)

T (°C)	t (s)	D ($\text{cm}^2 \text{ s}^{-1}$)
1856	1740	9.36×10^{-11}
1856	1740	7.24×10^{-11}
1922	1770	1.42×10^{-10}
1998	1170	2.62×10^{-10}
2080	870	6.94×10^{-10}
2172	870	6.04×10^{-10}
2268	570	1.50×10^{-9}
2381	570	2.49×10^{-9}
2381	570	2.92×10^{-9}

Cramer and Crow [1970] claim that the Gruzin method as applied in these experiments is only accurate for systems where radiation absorption is either very strong or very weak. However, there is no approximation involved in the derivation of equation (4.10). The only requirement is that the absorption should be exponential over the penetration distances involved. The alternative suggested by Cramer

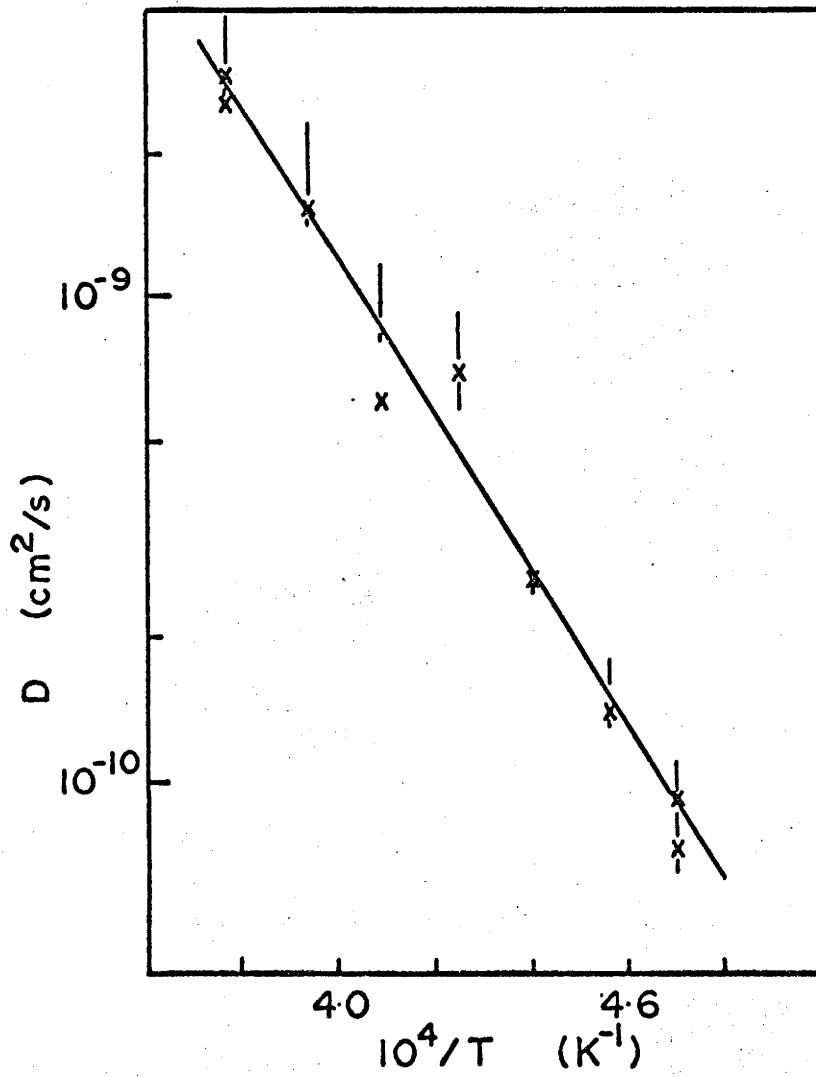


Figure 5.15. Arrhenius plot for Ca diffusion in single crystal MgO. Bars represent value limits calculated by the Cramer and Crow [1970] method.

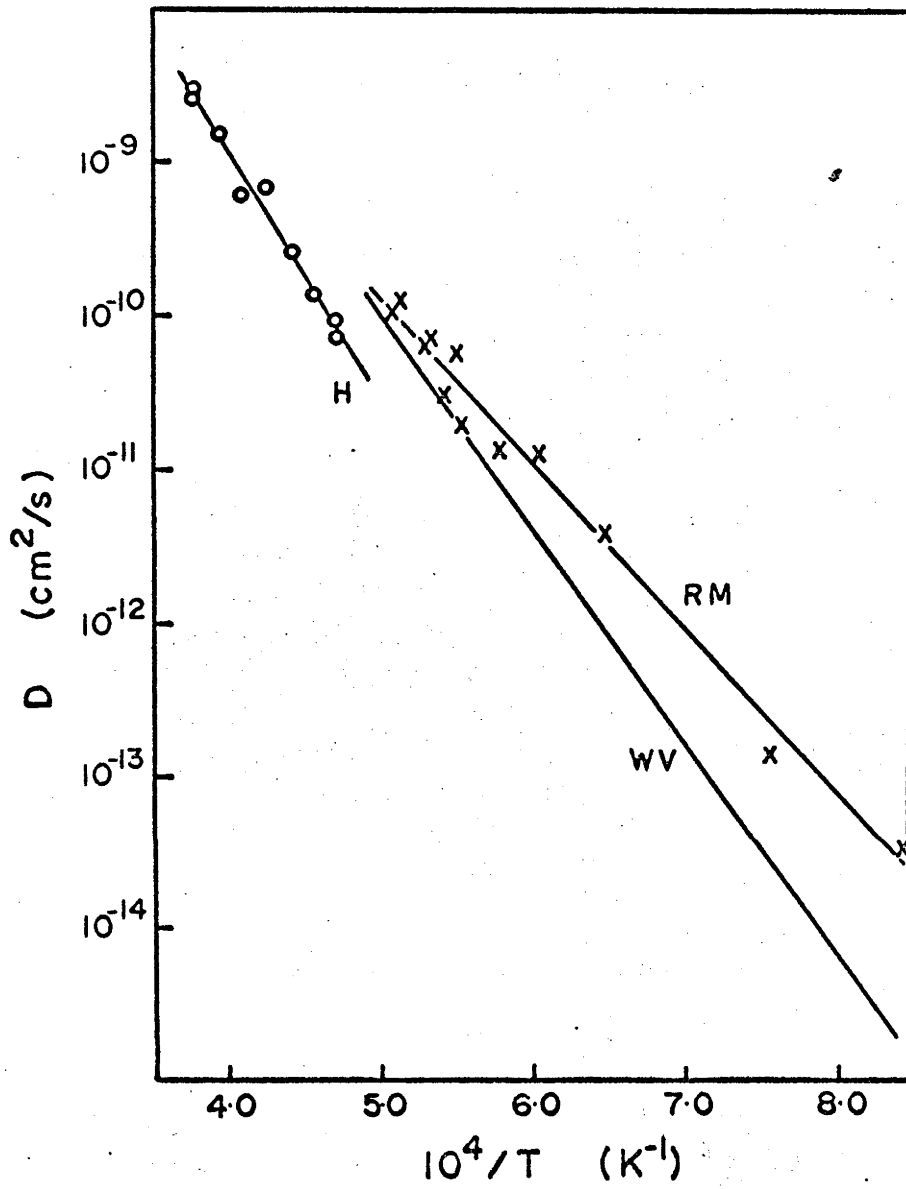


Figure 5.16. Arrhenius plot comparing Ca diffusion in MgO as measured by H - Harding [unpublished]; RM - Rungis and Mortlock [1966] and WV - Wuensch and Vasilos [1968].

and Crow involves carrying out the integration in equation (4.9) substituting (2.5) for $c(x)$. This gives

$$A_n = \frac{KM}{\sqrt{\pi Dt}} \exp \mu(x_n + \mu Dt) \operatorname{erfc}\{\mu\sqrt{Dt} + x_n/2\sqrt{Dt}\} . \quad (5.17)$$

When $x_n = 0$, then $A_n = A_0$ and

$$\frac{A_n}{A_0} = \exp \mu x_n \frac{\operatorname{erfc}\{\mu\sqrt{Dt} + x_n/2\sqrt{Dt}\}}{\operatorname{erfc}\{\mu\sqrt{Dt}\}} . \quad (5.18)$$

The diffusion coefficient can now be determined by plotting experimentally measured values of A_n/A_0 against x_n on detailed master graphs of this function (for various values of Dt) and selecting the proper Dt by comparison. This was done in the present case and the results are shown in figure 5.15. In most instances, only a range of D values could be extracted using this graphical method and these are plotted as bars on the graph. Allowing for this, it can be seen that the two methods of calculation give similar answers, as they should, although the points obtained using the Cramer and Crow method suggest that the activation energy and the pre-exponential factor may be a little higher (but still within error limits) than the values in equation (5.16).

5.6. Beryllium diffusion in MgO

Be^{2+} diffusion in magnesium oxide was previously studied in this laboratory in the temperature range 1000-1700 °C [Harding and Mortlock, 1966]. In this work, the temperature range was extended upwards to 2340 °C. Furthermore, in view of the more refined sectioning method used here, experiments were repeated in the lower range. Penetration profiles are shown in figure 5.17 where $\operatorname{erfc}^{-1} F(x)$ is plotted against x (Be^{2+} is readily soluble in MgO). Table 5.10 lists

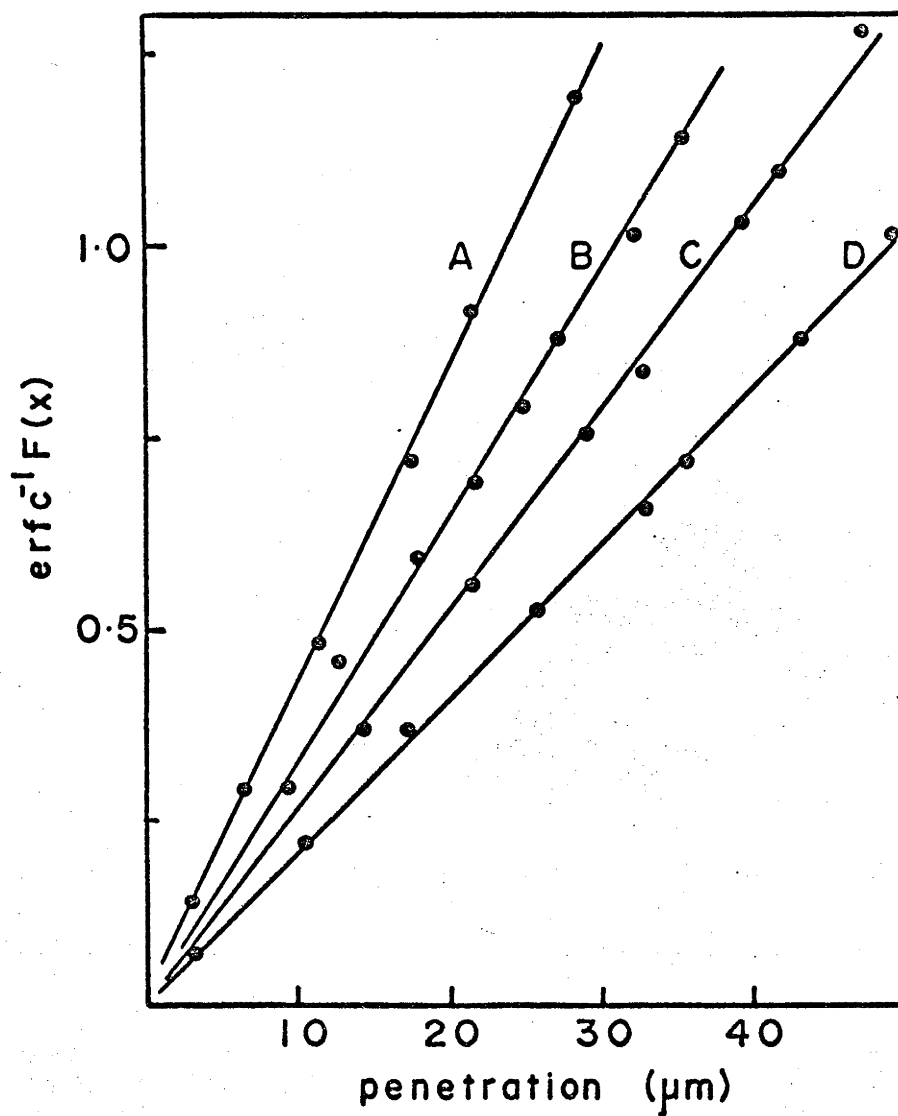


Figure 5.17. Penetration of Be-7 into single crystal MgO for various annealing conditions (argon atmosphere).

A - 1800 °C, 19m; B - 1977 °C, 15m; C - 2150 °C, 10m;
D - 2341 °C, 10m.

Table 5.10. Diffusion coefficients for Be^{2+} in single crystal MgO

T ($^{\circ}\text{C}$)	t (h or s)	D ($\text{cm}^2 \text{s}^{-1}$)	Atmos.
636	2000 h	3.29×10^{-14}	air
636	2000 "	1.46×10^{-14}	"
1016	113 "	4.66×10^{-12}	"
1016	113 "	5.10×10^{-12}	"
1118	52 "	1.45×10^{-11}	"
1118	52 "	1.30×10^{-11}	"
1213	17 "	4.33×10^{-11}	"
1213	17 "	3.89×10^{-11}	"
1326	7 "	1.08×10^{-10}	"
1326	7 "	8.48×10^{-11}	"
1467	2 "	2.82×10^{-10}	"
1467	2 "	3.17×10^{-10}	"
1647	3480 s	9.25×10^{-10}	"
1800	1140 "	1.38×10^{-9}	argon
1800	1140 "	1.37×10^{-9}	"
1903	1170 "	2.24×10^{-9}	"
1903	1170 "	2.01×10^{-9}	"
1977	810 "	2.90×10^{-9}	"
1977	810 "	2.70×10^{-9}	"
2058	870 "	3.80×10^{-9}	"
2150	600 "	6.36×10^{-9}	"
2150	600 "	6.12×10^{-9}	"
2233	585 "	9.69×10^{-9}	"
2233	585 "	7.89×10^{-9}	"
2341	600 "	1.33×10^{-8}	"
2341	600 "	1.03×10^{-8}	"

the measured diffusion coefficients for various times and temperatures of annealing. Two coefficients were obtained at 636 °C, but these points are not included in the Arrhenius plot (figure 5.18) because of scaling problems. Also, at this temperature, the solubility (estimated using equation (2.7)) was at least ten times smaller than at 1000 °C, and an excess of tracer was present on the MgO surface after annealing. Equation (4.7) was therefore used to determine the diffusion coefficient.

There are two factors which are noteworthy concerning these results. The first is that although there is a hint of structure in the Arrhenius plot, it is not as pronounced as in the Mg^{2+} , Ni^{2+} and Ba^{2+} diffusion data. Indeed a straight line can be drawn through all points in the temperature range 1000-2430 °C and this can be described by the least squares equation

$$D = \left(1.99 \begin{smallmatrix} + 0.24 \\ - 0.22 \end{smallmatrix} \right) \times 10^{-5} \exp[-(1.68 \pm 0.02) \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} \quad (5.19)$$

which compares favourably with the previously published result. Even the points at 636 °C are only a factor of 2-3 times the coefficient predicted for this temperature by equation (5.19) (i.e. $9.28 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$). It is interesting, however, that points above 1900 °C alone give a larger activation energy (2.0 eV), as do those below 1500 °C, (1.77 eV). The second point to be noted is that diffusion coefficients for Be^{2+} in MgO are at least an order of magnitude greater than the coefficients measured for other impurities and several times greater than the self-diffusion coefficients.

5.7. Germanium diffusion in MgO

With a few remaining MgO single crystals, several diffusion coefficients for Ge in MgO were measured in the temperature range

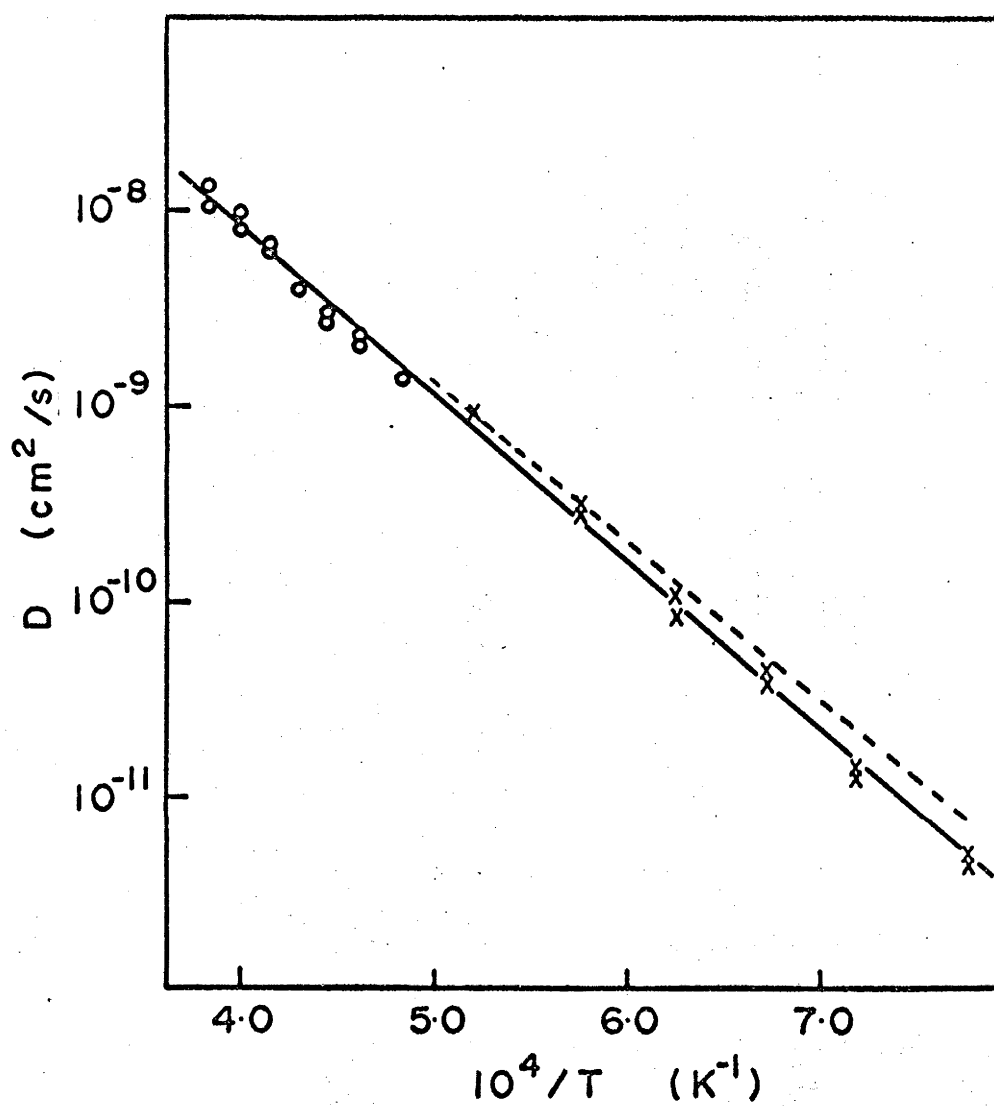


Figure 5.18. Arrhenius plot for Be diffusion in single crystal MgO.

- - Harding and Mortlock [1966];
- o - Argon annealing;
- x - Air annealing.

1860-2340 °C. At temperatures up to 2050 °C, it was found that germanium was not very soluble in MgO and equation (4.7) was used to evaluate D. (However, very nearly the same values were obtained using equation (4.5), though a large negative intercept on the x-axis resulted - see section 4.5.1.) Above 2050 °C, equation (4.5) was used as there was no evidence of a surface excess of tracer after annealing. In one experiment, at 2167 °C, the amount of tracer which dissolved in the host lattice was at least 20 times larger than in the other runs. The plot of $\operatorname{erfc}^{-1} F(x)$ vs. x in this case (figure 5.19) shows a curvature at small penetrations. Deeper within the crystal the line becomes straight, and D was calculated from this portion of the graph. This curvature could be due to a concentration dependence of D, as found for Sc^{3+} by Solaga and Mortlock [1970], although other factors previously discussed (section 4.5.2) may well be present. In the other runs, Ge concentrations were much less and linear $\operatorname{ierfc}^{-1} F(x)/1.772$ vs. x plots were obtained.

The Arrhenius plot for germanium diffusion in MgO is shown in figure 5.20 and the corresponding equation is

$$D = \left(0.34 \begin{array}{c} + 0.70 \\ - 0.23 \end{array} \right) \exp[-(4.0 \pm 0.2) \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1} . \quad (5.20)$$

Diffusion coefficients are given in table 5.11. The activation energy is significantly larger than values for divalent ions and it seems likely that germanium diffuses in MgO as Ge^{4+} .

It should be pointed out that the tracer used was carrier-free and since the total count obtained from a diffused sample was usually less than one per second, the data obtained refers to diffusion under very dilute conditions. This will be discussed further in the next chapter.

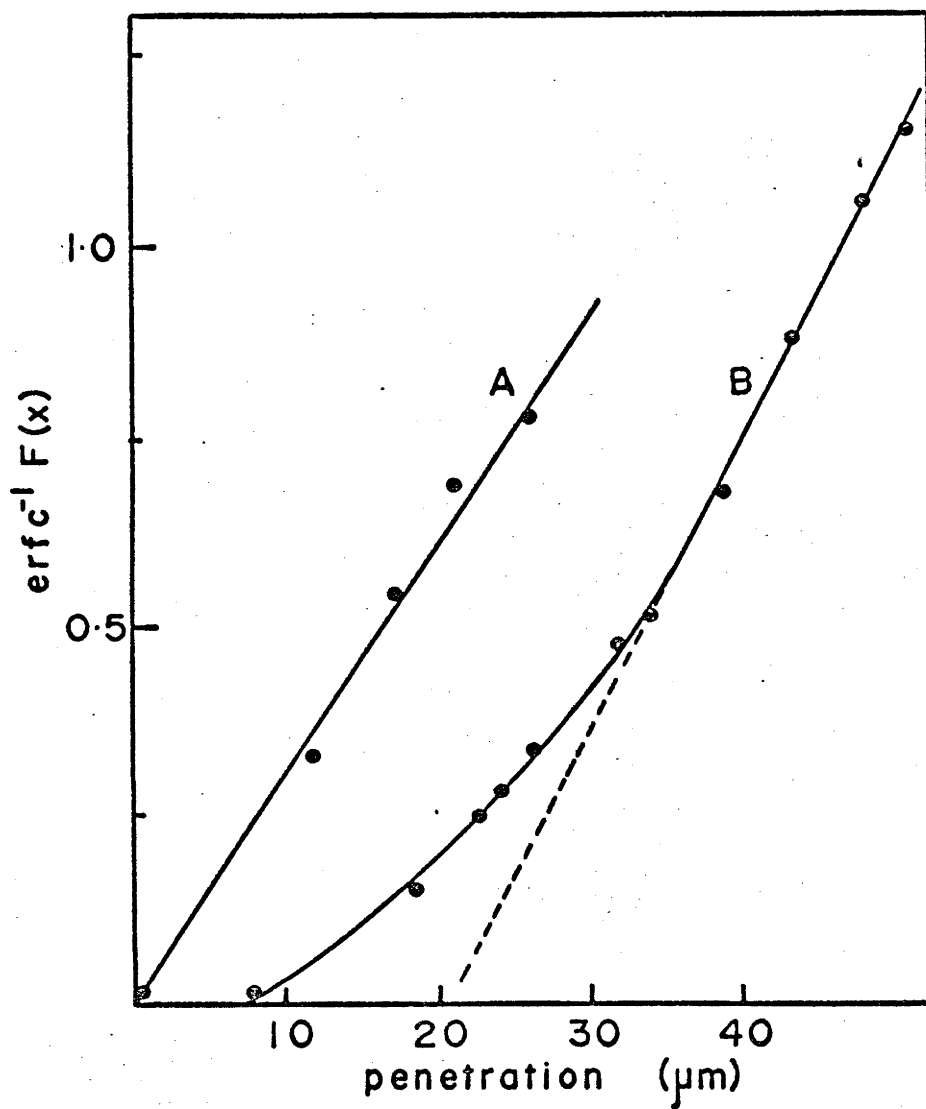


Figure 5.19. Penetration of Ge-68 into single crystal MgO.

A - 2343 °C, 580s; B - 2167 °C, 880s.

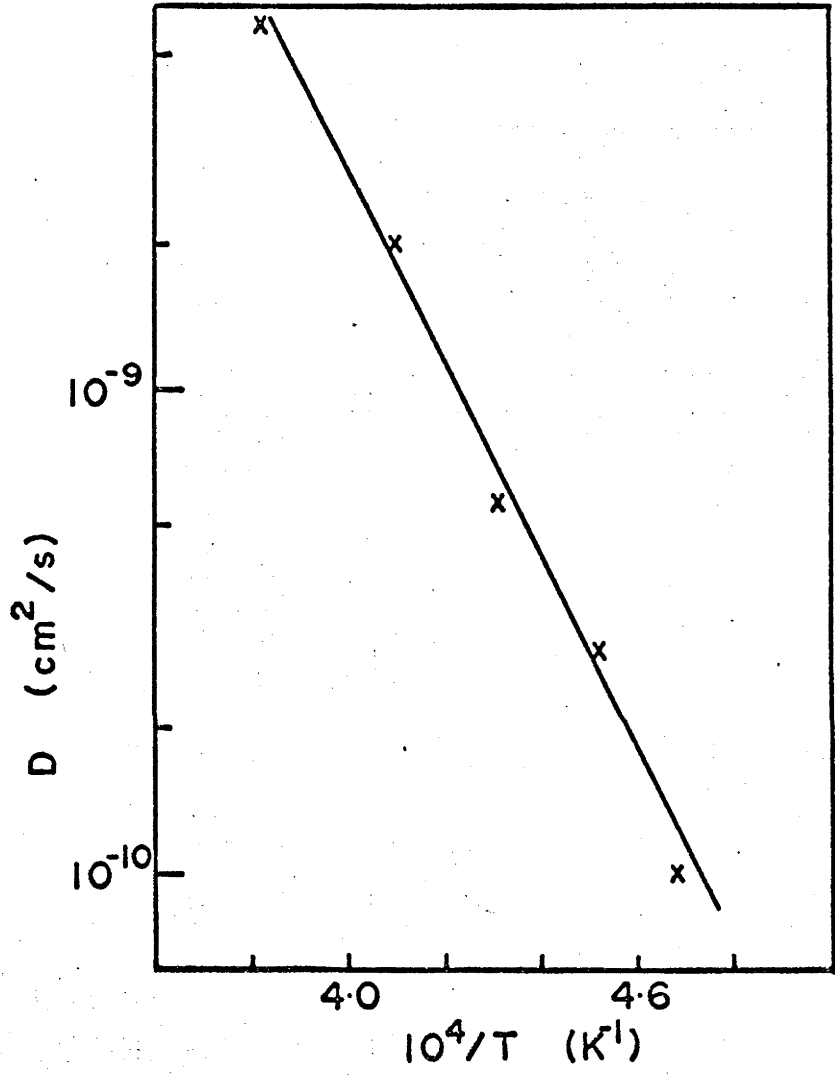


Figure 5.20. Arrhenius plot for Ge diffusion in MgO single crystals (v. dilute concentration).

Table 5.11. Diffusion coefficients for Ge^{4+} in
single crystal MgO (argon atmosphere)

T ($^{\circ}\text{C}$)	t (s)	D ($\text{cm}^2 \text{s}^{-1}$)
1863	1740	1.00×10^{-10}
1940	1170	2.89×10^{-10}
2048	870	5.77×10^{-10}
2167	880	2.00×10^{-9}
2343	580	5.74×10^{-9}

6. Discussion

6.1. Defect formation and migration in MgO

6.1.1. Theoretical calculations

Magnesium oxide, because of its rock-salt structure and strongly ionic character, has been generally accepted as a material in which Schottky disorder predominates at sufficiently high temperatures (cf. the alkali halides). However, attempts to calculate defect formation energies in oxides using the Mott-Littleton [1938] approach have not met with much success. Yamashita and Kurosawa [1954] found that oxygen-oxygen short-range interactions were attractive rather than repulsive, thus precluding the Born-Mayer treatment using ionic radii. Also, they found it necessary to assume that the polarisability of oxygen ions adjacent to a cation vacancy is about one third of the value for ions in perfect surroundings, in order to obtain even a small positive value for the energy of formation of a Schottky pair, h_s . The value of 4-6 eV often attributed to these authors was, in fact, an estimate based on a comparison with NaCl using the melting point correlation [Barr and Lidiard, 1970]. More recent calculations by Boswarva and Franklin [1968] agree with the findings of Yamashita and Kurosawa in principle. These authors obtained 2.1-2.9 eV for h_s , if only nearest-neighbour short-range interactions were considered, while if short range interaction parameters were derived from elastic constant data, they arrived at a value of 3.97 eV. The most recent attempt to calculate h_s has been by Boswarva [1972] and the values given are 9.07 eV and 10.09 eV.

It is possible to obtain h_s , and the enthalpies of formation for single ionised and neutral Schottky defects (h'_s and h_s^x respectively).

from a thermo-chemical-type calculation based on a series of possible solid state reactions in pure MgO. In theory, the heats of reaction required can be obtained from the band structure of MgO. Unfortunately, owing to the large Franck-Condon shift characteristic of polar crystals, it is impossible to deduce directly the equilibrium position of 'thermal' levels from optical absorption data. However, Kröger [1964], from a comprehensive review of available information, has arrived at reasonable estimates of the thermal energies required, for eight diatomic compounds. For the most ionic of these (KBr, KI) it was found that h_s^x was equal to the heat of sublimation, H_{sub} . The mean value of h_s^x/H_{sub} for all cases was greater than 0.8. Since MgO is strongly ionic, we shall assume h_s^x is equal to H_{sub} (10.3 eV). The reactions concerned are shown in table 6.1 together with Kröger's energy values for KBr and KI. For MgO, the energies E'_a , E_b^x and E_b^+ were calculated from the absorption energies of the V_1 , F and F^+ centres [see Henderson and Wertz, 1968; Kappers, Kroes and Hensley, 1970] using the equations given by Kröger [1964]. We have

$$\frac{E(\text{thermal})}{E(\text{absorption})} = \frac{(z/\kappa_s + 5c/16)^2}{(z/\kappa_s + 15c/16)(z/\kappa_s + 5c/16)} \quad (6.1)$$

where $c = 1/\kappa_o - 1/\kappa_s$ and κ_o , κ_s and z are the high frequency dielectric constant, the static dielectric constant and the effective charge on the ionised centre. The binding energy of a hole to a V_1 centre is estimated by Henderson and Wertz [1968] to be less than 1 eV. The value assigned here is $E'_a/2$.

The optical band gap of MgO is given by Reiling and Hensley [1958] as 8.7 eV. The difference between this and the thermal value was estimated from the difference between the emission and absorption energies of the F centres, allowing 0.7 eV for the dissociation energy of an exciton in MgO ($\approx 13.54/2\kappa_o^2$). In an alternative calculation, the

Table 6.1. Reactions used in the evaluation of formation energies for Schottky-type defects

Reaction	Energy (eV)		
	KI	KBr	MgO
$\text{nil} \rightleftharpoons e' + h' + E_i$	6.2	6.7	7.4
$\text{nil} \rightleftharpoons V_M^x + V_X^x + h_s^x$	5.31	6.04	10.3
$V_M^x \rightleftharpoons V_M' + h' + E_a^x$	1.18	0.94	0.7
$V_M' \rightleftharpoons V_M'' + h' + E_a'$	-	-	1.5
$V_X^x \rightleftharpoons V_X^\bullet + e' + E_b^x$	1.78	1.7	3.0
$V_X^\bullet \rightleftharpoons V_X^{\bullet\bullet} + e' + E_b^\bullet$	-	-	3.3
$\text{nil} \rightleftharpoons V_M' + V_X^\bullet + h_s'$	2.06	1.98	6.6
$\text{nil} \rightleftharpoons V_M'' + V_X^{\bullet\bullet} + h_s$	-	-	4.0

value obtained, using an elementary model [Mott and Gurney, 1948], agreed well with the first result. A mean value of 1.3 eV was taken, giving 7.4 eV for E_i . This, in fact, is not very different from twice the activation energy for electronic conduction (7.1 eV) obtained by Mitoff [1962].

Now from the reactions considered, we find that

$$h_s^x = h_s' + E_i - E_a^x - E_b^x \quad (6.2)$$

and

$$h_s' = h_s + E_i - E_a' - E_b^\bullet \quad (6.3)$$

Upon substitution, we obtain $h_s' = 6.6$ eV and $h_s = 4.0$ eV. Although these values are necessarily approximate, they do suggest that it is the enthalpy of formation of the singly ionised Schottky defect that should be compared, on the basis of melting point, with the alkali halides (in which, of course, such defects are singly ionised).

Frenkel defects have been regarded as unlikely to occur in MgO under normal conditions. A Mott-Littleton calculation, by Raux and Elston [1970], gave values for the formation enthalpies of cation and anion defects of 7.3 eV and 17.3 eV respectively. The same workers obtained an experimental value of (6.3 ± 1.6) eV from studies of Wigner energy release in MgO. If the conclusion, that Schottky disorder predominates in this material, is valid, then h_s must be somewhat lower than 6.3 eV.

It appears that no calculation of defect migration energies has been done for magnesium oxide. Lidiard [1967] estimates that Δh_m for both anion and cation vacancies is about 1.5 eV. More recently, a revised value of 2.5 eV has been given based on melting point comparisons [Barr and Lidiard, 1970].

6.1.2. Experimental information on defects in MgO

Experimental methods of determining the dominant defect in crystals include the evaluation of transport numbers from conductivity measurements, the comparison of pycnometric density changes with measurements of lattice constants using X-ray diffraction, and dielectric polarisation and loss experiments. Diffusion measurements in MgO suggest that the same mechanism is responsible for the motion of both magnesium ions and impurity cations, since the activation energies are of similar magnitude. Many impurities found in MgO are of similar size to the host cation and hence are easily accommodated substitutionally. Electron spin resonance experiments [e.g. Wertz and Auzins, 1957; Wertz, Orton and Auzins, 1962] have shown the existence of charge compensating vacancies in concentrations of up to 10^{17} per cm^3 in MgO, and the diffusion coefficient has been clearly shown to be dependent on the concentration of aliovalent ions in the lattice at

temperatures below 1700 °C [e.g. Solaga and Mortlock, 1970; Yamaguchi, 1969]. It is reasonable to conclude, therefore, that a vacancy mechanism operates for the diffusion of many impurities in MgO. However, it can be shown that very small cations, such as Be^{2+} , may feasibly be accommodated in the lattice on interstitial sites.

6.2. Self-diffusion in magnesium oxide

A summary of self-diffusion data for magnesium oxide is shown in figure 6.1. This includes the early Lindner and Parfitt [1957] results, the data reported here and the very recent information published by Wuensch, Steele and Vasilos [1972]. The oxygen diffusion data of Oishi and Kingery [1960] and Rovner [1966] are also shown, although both these studies were carried out using polycrystalline material. Conductivity results will not be considered because of the varying contribution of electronic processes to conduction.

For reasons already discussed, it appears that self-diffusion proceeds by a vacancy mechanism. There are three factors which must be considered when attempting to interpret the available experimental information. These are the presence of aliovalent impurities, the possible influence of oxygen partial pressure and the likely existence of intrinsic Schottky defects.

6.2.1. The effects of impurities on diffusion

Vacancies arise from the need for charge compensation in an ionic lattice and any factor which influences the concentration of aliovalent impurities may very well have an effect on diffusion. Such effects are illustrated in the data obtained from as-received tracer (ART) experiments, where there are two distinct slopes in the Arrhenius plot (equations (5.3) and (5.7)).

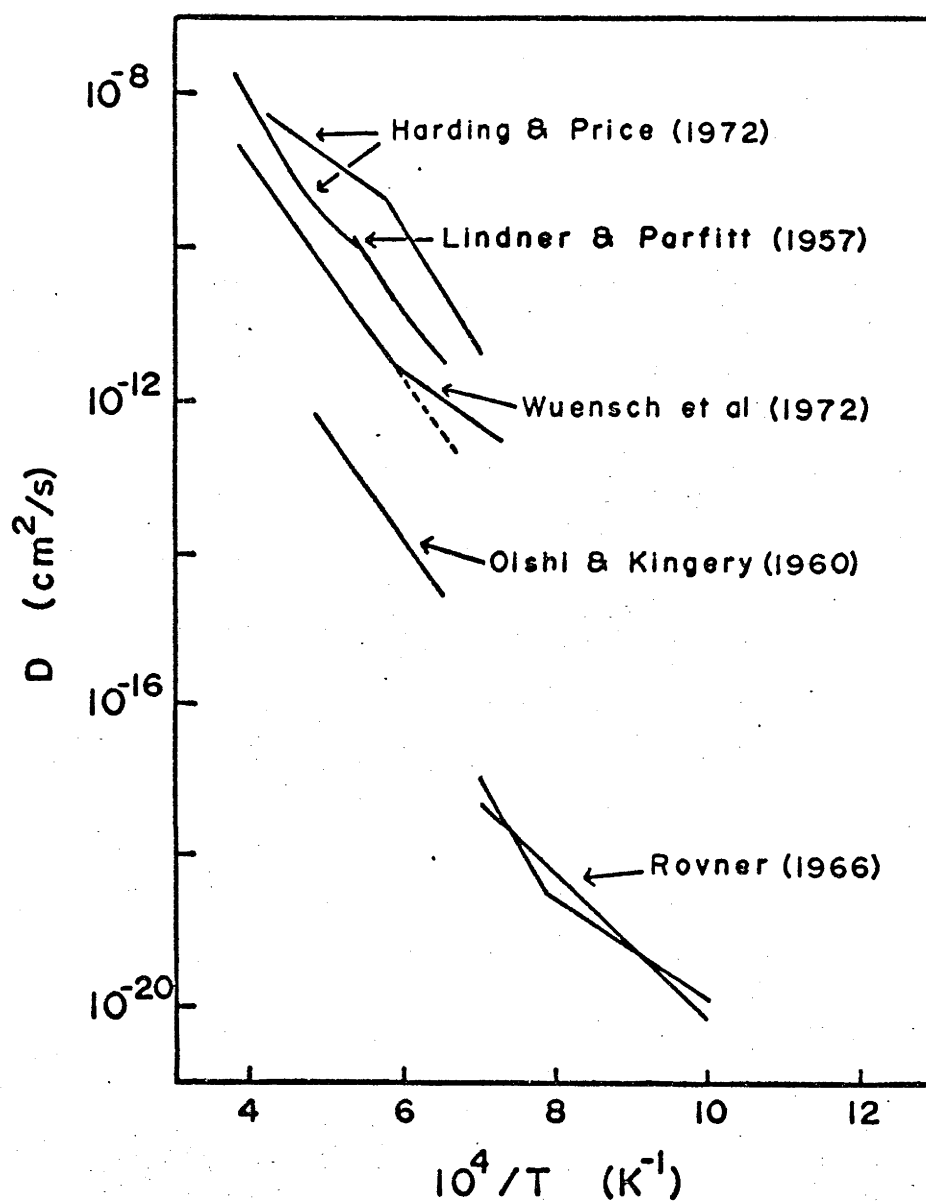


Figure 6.1. Summary of data for self-diffusion in MgO, including the oxygen diffusion results of Oishi and Kingery [1960] and Rovner [1966].

Impurity-vacancy association is known to occur in MgO [Glass, 1967; Glass and Searle, 1967; Wertz and Auzins, 1967; Crawford, 1970]. Work with the alkali halides shows that the effect on the Arrhenius plot is to produce a smooth curve concave to the origin, region III by convention [e.g. Kirk and Pratt, 1967; Hoodless, Strange and Wylde, 1971]. Reference to figure 5.2 shows that the downturn in the Arrhenius plot in this work is relatively sharp.

Impurity-precipitation is also well-established in MgO and apparently can occur even when concentrations are very low [Leipold, 1966; Srinivasan and Stoebe, 1970]. Barr and Lidiard [1970] point out that precipitation-controlled diffusion (region IV by convention) can be recognised by a sharp change in the slope of the Arrhenius plot, or by the superposition of diffusivities for samples containing differing amounts of impurity. The former requirement is satisfied in the results obtained here, but since the diffusion coefficients for ART and DT experiments do not coincide, the precipitating impurity cannot be aluminium alone. The most likely alternative is Fe^{3+} . Iron has been shown to be important in electrical conductivity [Mitoff, 1959, 1962] X-ray absorption [Soshea, Dekker and Sturtz, 1958] and precipitation strengthening [Srinivasan and Stoebe, 1970]. The diffusion studies of Yamaguchi [1969] also provide support for this suggestion. Figure 6.2, based on some of Yamaguchi's data, shows the diffusion coefficient of Ni in MgO, measured at 1450 °C, plotted against the molar concentrations (per cent) of Cr_2O_3 and Fe_2O_3 dopants. It can be seen that equal amounts of dopant produce very different enhancements of the diffusion coefficient. Both Cr^{3+} and Fe^{3+} can form associates with cation vacancies and it could be that the additional effect of precipitation is responsible for the relatively small enhancement produced by fairly large additions of Fe_2O_3 .

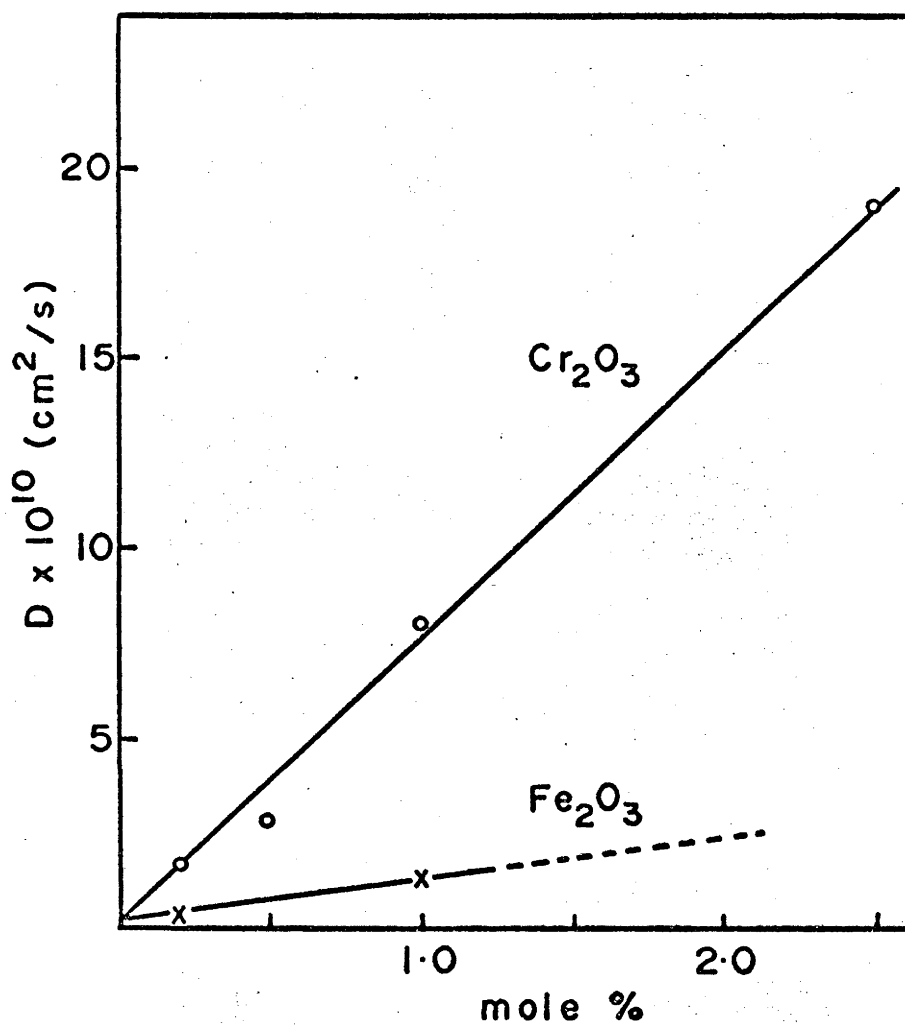


Figure 6.2. The enhancement of Ni diffusion in MgO doped with chromic and feric oxides at 1450 °C [Yamaguchi, 1969].

In view of these comments, it is suggested that the diffusion coefficients obtained below 1500 °C from ART experiments are precipitation-controlled and the activation energy (equation (5.3)) is equal to $\Delta h_m + h_d/3$. Above 1500 °C, the lower activation energy can be interpreted as being Δh_m alone, since the diffusion is still impurity-concentration dependent. It is therefore concluded from this data, that the enthalpy of motion of a cation vacancy is (1.56 ± 0.08) eV.

We turn now to the data obtained from the DT experiments and the results published by other workers. The simplest interpretation of the former is that they lie entirely in the extrinsic region and diffusion proceeds with an activation energy of 2.57 eV (equation (6.1)). The results of Wuensch et al. [1972] lead to an activation energy of 2.76 eV for a similar temperature range, while Lindner and Parfitt [1957] obtained 3.4 eV for the range 1400-1600 °C.

Wuensch et al. [1972] have taken their activation energy to be Δh_m , with D's for both Norton and Spicer MgO lying on the same line. However, table 4.1 shows that the vacancy concentrations arising from impurities in the two materials differ by a factor of more than ten. Even if all the iron were present as Fe^{2+} , and the work of Davidge [1967] and others implies that this is unlikely, there would still be a large difference between the Norton and Spicer crystals in this respect. This suggests that D is independent of sample purity. The activation energy cannot then represent only Δh_m .

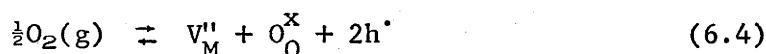
Another point to be noted is that at temperatures of 2100 °C and over, the ART and DT results obtained in this work coincide. Since there is a large purity difference between these two sets of samples, the implication is that D is intrinsic at these temperatures. This is definitely not so at temperatures below 1700 °C, say. There must, therefore, be a change to extrinsic diffusion at some point.

Again, if diffusion is impurity dependent over the entire temperature range, the data of Wuensch et al. for Norton MgO should lie above those obtained here, if the analysis given in table 4.1 is correct. It has already been pointed out that the Al^{3+} content of the Mg-28 tracer when diluted is negligible, and the suggestion by Wuensch et al., that the Si decay product contributes to the impurity level in this work, is untenable because of the low specific activities used.

Finally, if Δh_m is 2.57-2.76 eV, then it is difficult to explain the value of 1.56 eV obtained above, and the 3.4 eV obtained by Lindner and Parfitt between 1400 °C and 1600 °C.

6.2.2. Oxygen partial pressure and diffusion

Since the explanation of the self-diffusion measurements, in terms of extrinsic diffusion only, led to a number of difficulties, the possibility that the vacancy concentrations are controlled by oxygen partial pressure (p_{O_2}) must be considered. Reactions of the type



have been invoked to explain the dependence of conductivity in MgO [Osburn and Vest, 1970] and CaO [Duvigneaud and Wollast, 1970], and diffusion in SrO above 1450 °C [Murarka and Swalin, 1971] on p_{O_2} .

Calculation shows that below 1700 °C (where the DT experiments were performed in air) the difference between these results and those obtained by Wuensch et al. can be explained by an approximate $p_{\text{O}_2}^{1/6}$ dependence, as required by reaction (6.4). The activation energy in this case would represent $(\Delta h_m + H_f/3)$ where H_f is the heat of reaction (6.4). From the DT results, and using Δh_m equal to 1.56 eV, we obtain H_f equal to 3.0 eV. This however includes the energy of dissociation of an oxygen molecule in the gaseous phase (2.59 eV). Thus the energy

of formation of a doubly ionised cation vacancy would be 0.41 eV, an impossibly low value.

The Ni and Ba impurity diffusion studies below 1700 °C showed no dependence of D on p_{O_2} . The results for Ni also indicated that, in this temperature range, vacancy concentrations were impurity controlled. Wuensch and Vasilos [1962, 1971] found that the same Arrhenius equation could describe the diffusion coefficients for Ni in MgO in both air and argon. Furthermore, if an atmosphere effect did exist, the Arrhenius plot for the DT results for self-diffusion would show a discontinuity on changing to an argon atmosphere above 1700 °C. This would contradict the original assumption that equation (5.1) completely describes the results. The weight of evidence, therefore, seems to be against an atmosphere effect.

6.2.3. An interpretation involving Schottky defects

It was noted in section 6.2.1 that, at temperatures of 2100 °C and over, the results for ART experiments and DT experiments coincide indicating that D is independent of impurities. At 1900 °C and above, the DT results are described by equation (5.6) with a significantly greater activation energy operating. Since an atmosphere effect on D is unlikely, it is proposed that this activation energy represents $(\Delta h_m + h_s/2)$ and for a value of 1.56 eV for Δh_m , we obtain an enthalpy of formation of a Schottky defect of (3.8 ± 0.3) eV. A further inspection of the DT results leads to equation (5.8) for extrinsic (region II) diffusion.

The high activation energy obtained by Lindner and Parfitt [1957] has been attributed to intrinsic diffusion [Lidiard, 1967; Harding et al., 1971]. However, an analysis of MgO crystals from the same supplier as those used in the diffusion study (the Infra-red

Development Company) has been given by Clarke [1957] and it appears that Fe and Al were each present to 100 ppm. The Si content varied from 10 ppm for one sample to 400 ppm for another. Even taking the minimum impurity level, it is unlikely that intrinsic diffusion would be observed in the temperature range covered (1400-1600 °C). The data obtained in this work resolve the difficulty and show that these early results could well have related to region IV diffusion. Not only do the activation energies agree, but the diffusivities are in close accord also.

Using $h_s = 3.8$ eV, it is possible to calculate the entropy of formation, s_s , of a Schottky pair and the entropy of motion of a cation vacancy, Δs_m . The expressions for D in the intrinsic and extrinsic regions, respectively, are

$$D_s = \gamma a_o^2 \nu \exp(-g_s/kT) \exp(-\Delta g_m/kT) \quad (6.5)$$

and

$$D_e = \gamma a_o^2 \nu n_c \exp(-\Delta g_m/kT) \quad (6.6)$$

At a temperature well below the 'knee' between the two regions (≈ 1800 °C), n_c can be regarded as constant and equal to the vacancy concentration introduced by aliovalent impurities, n_i (60 ppm).

Dividing (6.5) by (6.6) eliminates γ , a_o , ν and Δg_m . Extrapolating the data described by equation (5.6) to a sufficiently low temperature, s_s is found to be 1.8 k. A similar value is obtained from the 'knee' temperature itself, where $n_i = n_o$. The entropy of motion can be calculated from the intrinsic and extrinsic pre-exponential factors if $\gamma \approx 1$, $\nu \approx 5 \times 10^{12} \text{ s}^{-1}$ and $a_o = 4.2 \text{ \AA}$. We obtain thus 1.2 k and 1.1 k respectively. The entropy of formation is, in fact, low compared with the alkali halides, but Δs_m is satisfactory. The self-consistency of these calculations is gratifying.

The data obtained by Wuensch et al. do not appear to fit into this interpretation of the results. The difference in activation energies may possibly be due to the relatively few data points measured by these workers. Assuming that Norton MgO indeed contains 120 ppm vacancies arising from impurities, the 'knee' temperature, based on the Schottky defect energies calculated above, should be about 1950 °C. Only four points were obtained above this temperature and any intrinsic effect could have passed unnoticed. At the lower end of the temperature range, dislocation enhancement in the presence of precipitation may have obscured the existence of region IV diffusion. Therefore, the 2.76 eV activation energy may well be an average for several processes. The low diffusion coefficients have still to be explained, however. In this respect two comments may be made regarding the experimental technique used by Wuensch et al. Firstly, a mass spectrometer was used to determine diffusion profiles, rather than a radio-isotope method. Secondly, diffusion couples were annealed for far longer times than were used in this study, and were encapsulated in pressed polycrystalline MgO, rather than a closed crucible, to prevent evaporation. Further experiments appear to be necessary to determine whether or not the discrepancy in diffusivities can be attributed to the different experimental methods used.

6.3. Divalent impurity diffusion in MgO

6.3.1. Nickel

The Arrhenius plot for Ni^{2+} diffusion in MgO shows the same features as were found in self-diffusion. The existence of a region II over a narrow range (1500-1900 °C) is confirmed by the experiments in which Al^{3+} was deliberately added to the tracer solution to simulate the conditions under which the ART results were obtained for self-

diffusion. Again, the onset of region IV diffusion is accompanied by a small enhancement by a short-circuit mechanism, and over regions II and IV no difference in diffusion coefficient was produced by a change of atmosphere from air to argon. From the activation energies in equations (5.9) and (5.10), the formation energy of a Schottky defect pair is 3.4 eV. Within error limits, this value is in satisfactory agreement with that obtained in self-diffusion. The temperature dependence of the correlation factor should be negligible, since Δh_m for Ni^{2+} diffusion is very close to that for Mg^{2+} motion.

Another study of Ni^{2+} diffusion in MgO has been made over a similarly wide temperature range by Wuensch and Vasilos [1971], using an electron microbeam probe to determine diffusion profiles. Although this was not a tracer study, Blank and Pask [1969] have shown that the activation energy for diffusion does not vary with concentration, at least at lower temperatures (1200-1400 °C). Wuensch and Vasilos claim that one equation describes their data over the entire temperature range, namely equation (5.12). However, a least squares calculation of their data above 1900 °C gives an activation energy of (3.26 ± 0.25) eV for Norton crystals alone, and (2.93 ± 0.24) for both Norton and Spicer MgO . Both types of material again gave diffusion coefficients that agreed closely, showing that diffusion at these temperatures is not impurity controlled. Not only do these higher activation energies agree with that in equation (5.9), but in this case, the diffusivities are also in reasonable agreement with the data obtained in this study. To ignore the structure in the Arrhenius plot and use equation (5.11) to describe all data in the temperature range 1100-2500 °C leaves the lower activation energy obtained with the doped system (1.6 eV) unexplained.

The mass spectrometric study by Yamaguchi [1969] has been mentioned previously. Over the temperature range 1400-1550 °C, the activation energy for Ni^{2+} diffusion in MgO ranged between 3 eV and 4 eV for 'pure' MgO and MgO doped with Fe^{3+} , Cr^{3+} and Co^{2+} . Allowing for the narrow temperature range, these E values agree with the region IV activation energy found here (3.2 eV). Furthermore, the diffusivities obtained for 'pure' MgO agree well with the present data.

6.3.2. Barium, calcium and cadmium

The investigation of barium diffusion in MgO reported here appears to be the only work done with this tracer. Figure 5.9 includes some of the data published by Harding [1967a] and it is now apparent that this represented region IV diffusion. The arguments presented for a structured Arrhenius plot can again be applied here, although the data is more scattered than for Ni^{2+} and Mg^{2+} , because of the difficulties caused by the extremely low solubility of the tracer. The 'knee' temperature between regions I and II is in approximate agreement with the values found in the Ni^{2+} and Mg^{2+} experiments.

The calcium and cadmium [Harding and Bhalla, 1971] diffusion studies are both apparently in the intrinsic region, but it is interesting to note that although the activation energies are in agreement within error limits, the pre-exponential factor for Ca^{2+} is considerably lower than that for Cd^{2+} . This will be mentioned again later.

Two other studies of Ca^{2+} diffusion have been made by Wuensch and Vasilos [1968] and Rungis and Mortlock [1966]. The temperature range covered by Wuensch and Vasilos was 800-1850 °C and the data are described by

$$D = 8.9 \times 10^{-4} \exp[-2.76 \text{ eV}/kT] \text{ cm}^2 \text{ s}^{-1} . \quad (6.7)$$

However, there is considerable scatter in these results, particularly below 1300 °C.

Rungis and Mortlock [1966] used an autoradiographic method to measure Ca-45 diffusion in MgO and obtained diffusion coefficients given by

$$D = \left(2.95 \begin{smallmatrix} + 2.6 \\ - 1.5 \end{smallmatrix} \right) \times 10^{-5} \exp[-(2.13 \pm 0.1) \text{ eV/kT}] \text{ cm}^2 \text{ s}^{-1} . \quad (6.8)$$

Above 1300 °C, these data do not differ greatly from those of Wuensch and Vasilos, but at lower temperatures, diffusion coefficients are as much as a decade higher. The difference between the two sets of results could be explained by differing degrees of crystal lattice damage, since this would be less important at higher temperatures. In this regard, it is worth noting that the cylindrical samples used by Rungis and Mortlock had been core-drilled from a larger piece of MgO. Neither of the activation energies is very close to that predicted for extrinsic diffusion (region II) from the high temperature results obtained in this study (1.3 eV).

6.3.3. Beryllium

The data for beryllium diffusion differ from the results for the other tracers studied in that a single Arrhenius equation adequately describes the diffusion coefficients (equation (5.19)). In addition, there is very much less scatter in the data points, the solubility is very much greater for Be^{2+} than for the other tracers, and diffusivities are very much higher than even those for self-diffusion. The points at 636 °C show very little enhancement over the value predicted by equation (5.19). All these factors are consistent with the suggestion that beryllium diffuses interstitially. Unfortunately, an isotope effect experiment failed because of the low specific activity of the

available Be-10 tracer. Further experiments to check this proposal using alternative methods would be of interest.

The activation energy above 1900 °C appears to increase by a few tenths of an eV as the coefficients measured for the other tracers approach those obtained for Be^{2+} in magnitude ($\sim 10^{-8} \text{ cm s}^{-1}$), and at the highest temperatures, it may well be that a vacancy mechanism becomes energetically more favourable.

6.3.4. Other divalent ions

The diffusion of strontium in MgO has been investigated using Sr-85 in the temperature range 1000-1630 °C by Mortlock and Price [1972] and the activation energy obtained was 2.91 eV. As with barium, difficulties were encountered because of low solubility and low diffusion coefficients. Most profiles showed the existence of short-circuit diffusion and were similar to those shown in figure 5.10 for barium. It is suggested that these results relate mainly to region IV diffusion - in fact, the activation energy below 1400 °C is 3.2 eV, in excellent agreement with the values for Mg^{2+} , Ni^{2+} and Ba^{2+} . On this basis, the activation energies for Sr^{2+} diffusion in regions I and II would be 3.5 eV and 1.6 eV respectively.

A summary is given in table 6.2 of a large number of diffusion studies in MgO. Low temperature data could be subject to dislocation influences (see section 6.6). Many of the investigations were in the field of chemical diffusion and for this reason, pre-exponential factors have been omitted as they usually vary with concentration. On the other hand, activation energies were often found to be concentration independent. The majority of ions listed are divalent, but the results for several aliovalent ions are included and these will be discussed in section 6.5.

Table 6.2. Summary of diffusion in MgO single crystals

Ion	δ (eV)	T range ($^{\circ}\text{C}$)	Reference
Mg^{2+}	3.46	1900 - 2340	Harding and Price [1972]
	1.56	1540 - 1800	" "
	3.2	1130 - 1540	" "
	2.76	1450 - 2400	Wuensch et al. [1972]
	3.4	1400 - 1600	Lindner and Parfitt [1957]
O^{2-}	2.71	1300 - 1750	Oishi and Kingery [1960]
	3.63	1580 - 1750	" "
	3.57	1000 - 1150	Rovner [1966]
	1.39	750 - 1000	"
	1.85	750 - 1150	"
Ni^{2+}	3.33	1900 - 2500	Harding [1972]
	1.64	1500 - 1800	"
	~ 3.2	1100 - 1500	"
	2.10	1000 - 2400	Wuensch and Vasilos [1971]
	[†] 3.26	1900 - 2400	" "
Ba^{2+}	1.87	1200 - 1400	Blank and Pask [1969]
	3.46	1900 - 2445	Harding [1972]
	1.56	1500 - 1800	"
	3.31	1000 - 1500	"

[†] - re-calculated.

(continued over)

Table 6.2 (continued)

Ion	δ (eV)	T range ($^{\circ}\text{C}$)	Reference
Ca^{2+}	3.2	1850 - 2380	Harding [unpublished]
	2.13	900 - 1700	Rungis and Mortlock [1966]
	2.76	790 - 1850	Wuensch and Vasilos [1968]
Cd^{2+}	3.4	1850 - 2270	Harding and Bhalla [1971]
Be^{2+}	1.68	1000 - 2400	Harding [unpublished]
Sr^{2+}	2.91	1000 - 1630	Mortlock and Price [1972]
Fe^{2+}	1.98	1300 - 1700	Tagai et al. [1965]
	1.81	1000 - 1800	Wuensch and Vasilos [1962]
	1.29	1150 - 1350	Blank and Pask [1969]
Co^{2+}	2.06	1000 - 1800	Wuensch and Vasilos [1962]
Mn^{2+}	1.22	1300 - 1700	Tagai et al. [1965]
	1.78	1380 - 1570	Jones and Cutler [1971]
Zn^{2+}	1.85	1000 - 1650	Wuensch and Vasilos [1965]
Cr^{3+}	2.96	1300 - 1700	Tagai et al. [1965]
	2.91	1340 - 1550	Greskovich and Stubican [1970]
Al^{3+}	3.30	1580 - 1860	Whitney and Stubican [1971]
Y^{3+}	3.10	1400 - 1760	Berard [1971]
Fe^{3+}	3.24	1000 - 1460	Blank and Pask [1969]
Sc^{3+}	2.19	1200 - 1765	Solaga [1972]
Ge^{4+}	4.0	1860 - 2340	Harding [unpublished]

6.4. Factors influencing divalent ion diffusion in MgO

The three factors in the expression for the diffusion coefficient which are likely to depend on the properties of the diffusing ion and its host lattice are activation enthalpy, activation entropy and the vibrational frequency, ν . The first of these is determined from the slope of the Arrhenius plot, while the second and third occur in the pre-exponential factor. Two sets of data will be discussed in this section, one derived by assuming that diffusion in MgO can be represented by non-structured Arrhenius plots and the other derived from structured Arrhenius plots.

6.4.1. Non-structured Arrhenius plots

Table 6.3 lists the parameters obtained for the diffusion of a number of ions in MgO, together with the respective ionic radii and TKS polarisabilities. The data obtained by Wuensch, Steele and Vasilos [1972] for Mg^{2+} diffusion, and Wuensch and Vasilos [1971] for Ni^{2+} diffusion, both in Norton and Spicer crystals, are included. The Ca^{2+} results include those measured by Rungis and Mortlock [1966] in Monocrystals MgO, the same material being used also by Price and Mortlock [1972] in the Sr^{2+} studies.

It is difficult to find any regular correlation in the data as presented, but there is a trend in both activation energy and pre-exponential factor towards higher values with increasing ionic radius. This agrees with the correlation proposed by Mortlock [1968] between activation energy for diffusion and the square of the ionic radius, r . Mortlock [1968] also suggested that $\log D_0$ should increase linearly with r^3 . However, the new data covering an extended temperature range do not show these relations as well as did the earlier low temperature parameters. A graph of $\log D$ plotted against ionic radius, given

Table 6.3. Diffusion of impurities in MgO assuming non-structured Arrhenius plots. Ionic radius (r) and polarisability (α) are compared with ϵ and D_o .

Ion	r (Å)	α (Å ³)	ϵ (eV)	D_o (cm ² s ⁻¹)	T range (°C)
Ba ²⁺	1.34	2.5	2.97	2.98×10^{-3}	1000-2500
Be ²⁺	0.35	(0.008)	1.68	1.92×10^{-5}	1000-2500
** Ca ²⁺	0.99	1.1	2.02	1.21×10^{-5}	1000-2500
Cd ²⁺	0.97	1.8	3.44	1.72×10^{-2}	1780-2300
Mg ²⁺	0.66	0.1	2.57	8.59×10^{-4}	1200-2500
† Mg ²⁺	0.66	0.1	2.76	4.19×10^{-4}	1100-2400
Ni ²⁺	0.69	0.25	2.41	1.86×10^{-4}	1100-2500
† Ni ²⁺	0.69	0.25	2.10	1.80×10^{-5}	1000-2500
* Sr ²⁺	1.12	1.6	2.91	6.07×10^{-4}	1000-1630

† Wuensch, Steele and Vasilos [1972]

† Wuensch and Vasilos [1971]

* Mortlock and Price [1972]

** Includes data by Rungis and Mortlock [1966].

previously by Mortlock [1970], is reproduced in figure 6.3 for data obtained at 1000 °C, 1500 °C and 2000 °C. The solid curves are based on the linear relations, between ϵ and r^2 , and $\log D_o$ and r^3 , mentioned above. The experimental points fit these curves quite well at 1000 °C and 1500 °C, but at 2000 °C they deviate increasingly from the predicted values. On this basis, it could conceivably be argued that the original assumption of a single line Arrhenius plot is incorrect.

Mortlock [1968, 1970] argues that the shape of the curves in figure 6.3 arises from the elastic-strain energy necessary to overcome

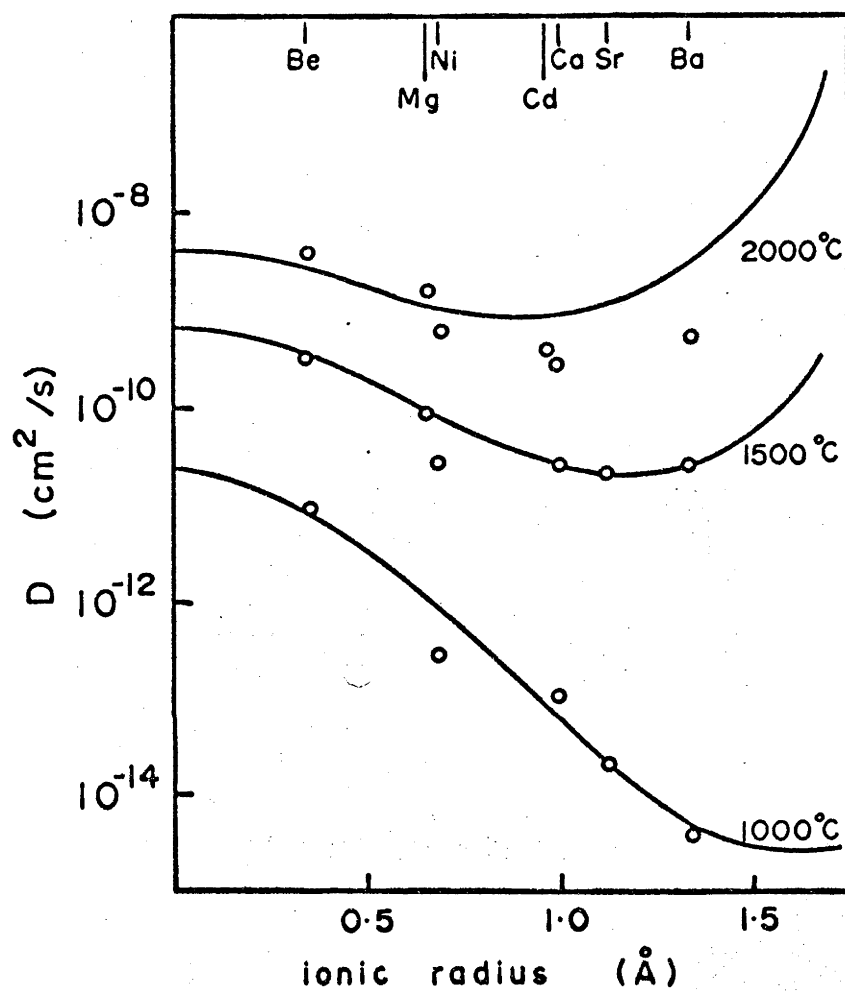


Figure 6.3. Variation of $\log D$ with ionic radius of the diffusing divalent ion in MgO [after Mortlock, 1970].

the potential barrier opposing a diffusion jump, coupled with an entropy contribution. This entropy contribution derives from the disorder introduced into the lattice during a jump and depends on the size of the impurity ion. It is this factor which produces the up-swing in the curves as r increases, overcoming the decreased probability for jumping produced by the increasing height of the enthalpy barrier opposing diffusion. However, this last effect is yet to be confirmed by experiment.

6.4.2. Structured Arrhenius plots

Taking firstly the activation energies measured above 1900 °C (i.e. in region I) for all ions except Be^{2+} and plotting them against ionic radius (figure 6.4), it can be seen that within the limits of the least squares standard errors, δ is independent of the radius of the diffusing impurity. The value for Sr^{2+} is based on the region IV activation energy. If $h_s/2$ is added to the activation energies obtained in other studies of Fe^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} diffusion in MgO (see table 6.2), these also fit this conclusion reasonably well, although some scatter is introduced because the measured values of δ are probably not equal to Δh_m alone. This absence of any detectable effect of ionic radius on intrinsic activation energy is similar to the result found for various monovalent impurities in NaCl [Chemla, 1954; Bènière, Bènière and Chemla, 1969] and KCl [Arnikar and Chemla, 1956]. The fact that Be^{2+} shows an activation energy much smaller than the other divalent ions may indicate a different mechanism of diffusion.

Since the values for $(\Delta h_m + h_s/2)$ are equal within present experimental error, it follows that Δh_m must also be independent of r and an average value for the divalent ions studied here (including Sr^{2+}) is found to be 1.5 eV.

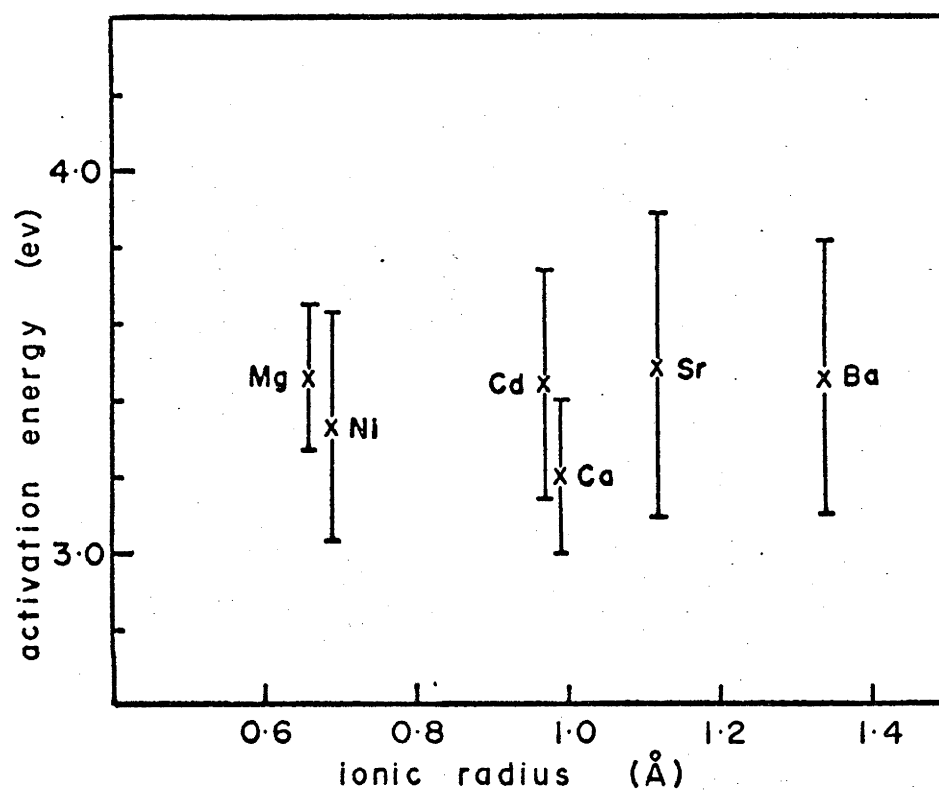


Figure 6.4. Activation energy for intrinsic diffusion of divalent cations in single crystal MgO as a function of ionic radius.

A graph of the intrinsic pre-exponential factor against ionic radius (figure 6.5) is more difficult to assess. The point for Ca^{2+} could be too low because the activation energy measured was below average. The measured D 's, in fact, were only 40% lower than those for Cd^{2+} . If this is so, it would appear that D_0 for divalent ion diffusion in MgO is also little affected by r .

A more interesting picture emerges if D_0 is plotted against the TKS polarisability of the diffusing impurity. In figure 6.6, a logarithmic scale is used and a smooth curve is drawn through the data points. However, the use of a linear scale shows that for the larger ions, D_0 is directly proportional to the polarisability. The importance of polarisability was suggested in an early study by Wuensch and Vasilos [1962], and Laurent and Bénard [1958] found that polarisability directly influenced dislocation enhanced diffusion in the alkali halides. This result does not extend to Ni^{2+} and Mg^{2+} which have very small polarisabilities, and in these cases the competing effect of mass appears to be dominant. Although the ratio of the respective pre-exponential factors is larger than would be expected, this could be accounted for by the standard errors which, as is usual, are rather large. If the corresponding extrinsic (region II) parameters are compared, assuming a common 'knee' temperature of 1800°C , the ratio of the D_0 's for Mg^{2+} and Ni^{2+} is much closer to the expected value, while the linear relation between α and D_0 for the larger ions is even more pronounced. Apart from this, the appearance of the graph is very similar to figure 6.6.

Summarising, it can be said that the 'hard sphere' ionic radius has little or no detectable effect on the activation energy for diffusion. Insofar as it is closely related to polarisability, 'size' does affect D_0 and hence the measured value of D . For ions of small

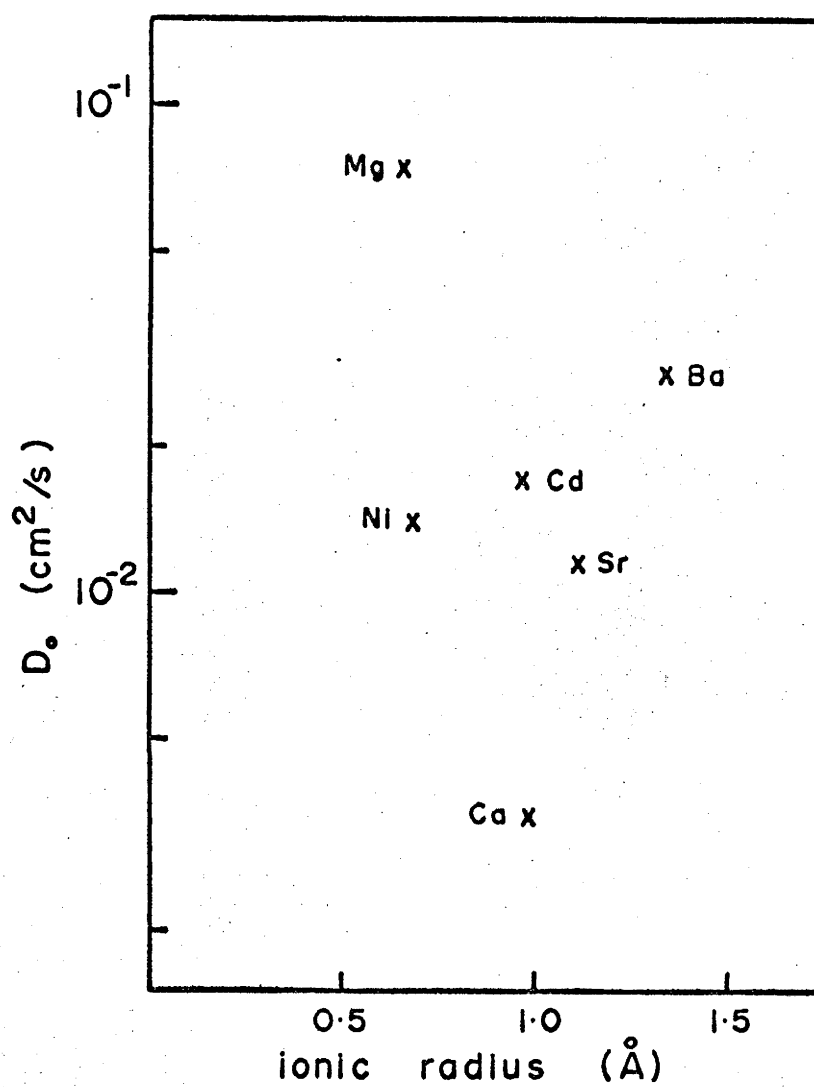


Figure 6.5. Pre-exponential factor for intrinsic diffusion of divalent cations in single crystal MgO as a function of ionic radius.

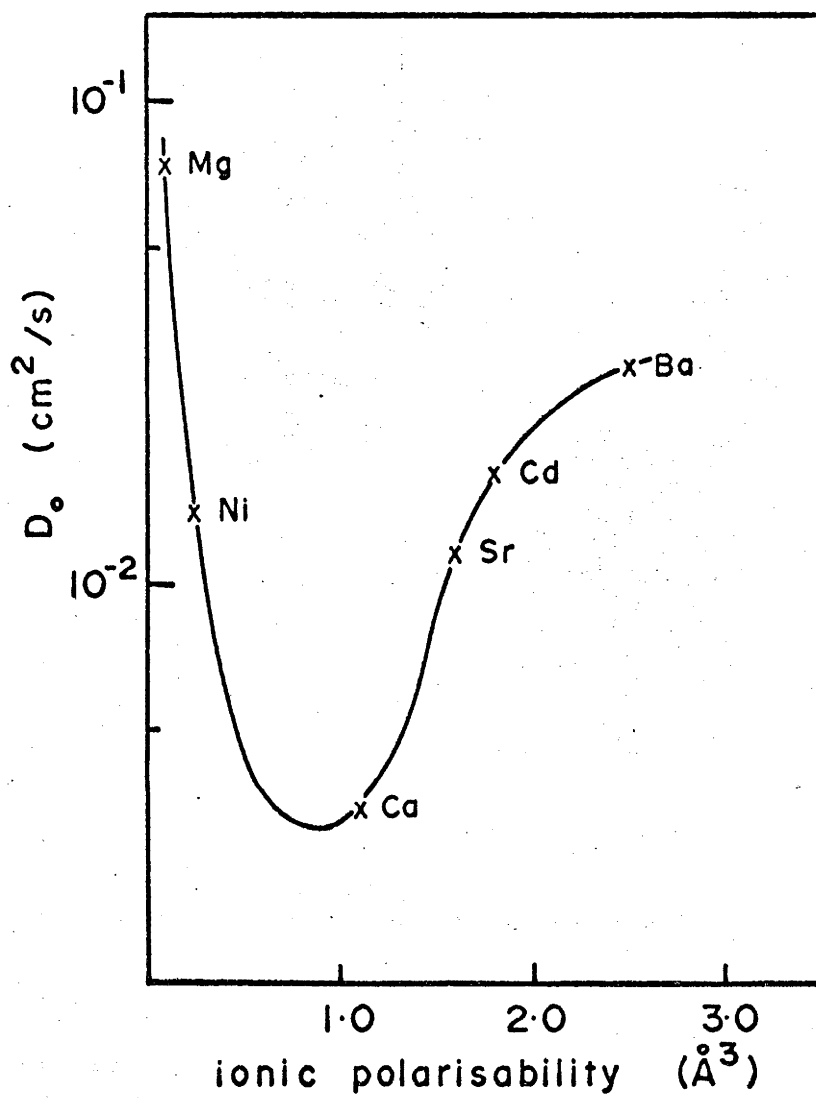


Figure 6.6. Pre-exponential factor for intrinsic diffusion of divalent cations in single crystal MgO as a function of ionic polarisability.

polarisability it is suggested that increasing mass leads to a decrease in D_0 through the vibrational frequency term. For larger ions, increasing polarisability leads to an increase in D_0 and this could occur either through v , or the entropy factor.

6.4.3. A summary

Both of the interpretations given above show that measured values of the diffusion coefficient depend on ionic 'size'. However, section 6.4.1 suggests that this effect operates through ϵ as well as D_0 , whereas the discussion in section 6.4.2 leads to a size-independent enthalpy of motion, with the size effect operating through D_0 via polarisability. In view of the scattered nature of the data in table 6.3, the apparent breakdown of the correlation proposed by Mortlock at high temperatures and the arguments put forward in section 6.2, the second interpretation based on structured Arrhenius plots seems preferable.

6.5. The diffusion of aliovalent cations in MgO

The theory of diffusion of aliovalent ions in the alkali halides has been treated by Friauf [1969] and Lidiard [1955a, 1955b, 1957]. For the first association of trivalent ions with vacancies in MgO, and for the association of four-valent ions and vacancies we can write, from the law of mass action

$$n_k [n_c (c - n_k)]^{-1} = K(T) \quad (6.9)$$

where the notation is similar to that used in section 3.2. In terms of the degree of association, β , equation (6.9) becomes

$$\beta(1 - \beta)^{-1} = n_c K \quad (6.10)$$

with $\beta = n_k/c$. Solving for β we have

$$\beta = n_c K (1 + n_c K)^{-1} . \quad (6.11)$$

It can be shown that the diffusion coefficient for the introduced aliovalent ion is a function of concentration and is given by

$$D(c) = D^0 [d(\beta c)/dc] \quad (6.12)$$

where D^0 is given by equation (2.22).

The coulomb binding energy of a trivalent ion to an Mg^{2+} vacancy in MgO is 1.0 eV, while the measured value for Cr^{3+} -vacancy association is approximately 0.8 eV [Glass, 1967]. These energies compare favourably with the 0.5 eV binding energy for divalent ion-vacancy associates in NaCl [Barr and Lidiard, 1970] reflecting the fact that although the dielectric constant is larger for MgO, the nearest neighbour distance is smaller. Taking a value of 0.9 eV and assuming purely coulombic forces, the binding energy for a four-valent ion and a vacancy is estimated to be 1.8 eV. The entropy of association has been found by Crawford [1970] to be fairly high and an average of his values is 5.4 k (including the orientational degeneracy factor, $-\ln 12$).

The activation energy for germanium diffusion in MgO over the temperature range 1850-2350 °C was (4.0 ± 0.2) eV, that is, significantly greater than the values for divalent ions in the same temperature range. Therefore, it is concluded that germanium diffuses as Ge^{4+} rather than Ge^{2+} . Because the tracer used was carrier free and the count rates very low, it is valid to assume that the vacancy concentration n_c in (6.11) is dominated by the Schottky defect concentration, n_o . Using the formation enthalpy and entropy deduced in section 6.2.3 to calculate n_o and the above values for h_k and s_k we find that $n_o K \ll 1$. Therefore, in the intrinsic region $\beta \approx n_o K$. This agrees with Lidiard's conclusion

for the alkali halides and the activation energy for diffusion represents $(\Delta h_m + h_s/2 - h_k)$ [Barr and Lidiard, 1970]. With $h_k \approx 1.8$ eV, we find that the vacancy-impurity exchange enthalpy, Δh_m , is 3.9 eV.

For a trivalent ion at high concentrations ($c \gg n_o$ or $c \gg n_i$) it can be shown that both β and $d(\beta c)/dc$ approach unity and

$$D(c \rightarrow \infty) = D^0. \quad (6.13)$$

Hence the measured activation energy for diffusion gives Δh_m . This seems to be the case for the Cr^{3+} , Al^{3+} , Y^{3+} and Fe^{3+} data listed in table 6.2. Again, there appears to be little variation of ϵ with ionic radius and an average value of Δh_m is 3.1 eV.

It is apparent from these results that Δh_m is strongly influenced by the charge on the diffusing ion. This is to be expected, since the ion has to pass through a ring of negatively charged oxygen ions to complete a jump. An empirical correlation between the electronic charge and Δh_m is shown in figure 6.7. A straight line, within error limits, is obtained when charge is plotted on a logarithmic scale against Δh_m and this relationship is approximately given by

$$q = A \exp(\Delta h_m/4) \quad (6.14)$$

where A is a constant.

Under conditions where a diffusing aliovalent species is present in very small concentrations ($c \ll c_i$) equation (6.11) reduces to

$$\beta = \frac{1}{2}c_i K = n_i K. \quad (6.15)$$

The activation energy for extrinsic diffusion is then given by $(\Delta h_m - h_k)$. The result obtained by Solaga [1972] is in agreement with the expected value (namely $3.1 - 0.9 = 2.2$ eV). However, no significant

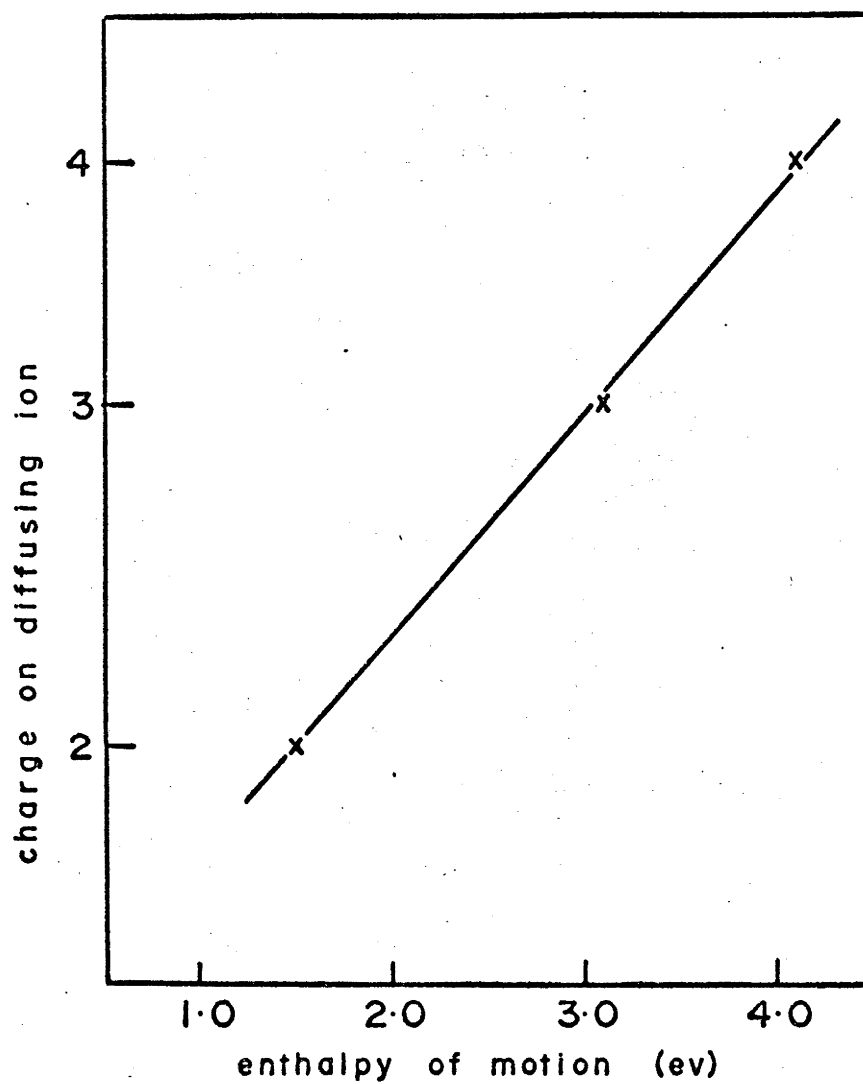


Figure 6.7. An empirical relation between the enthalpy of motion in MgO of a diffusion impurity cation and its actual electronic charge.

change in δ was detected over the temperature range 1200-2100 °C, and like the self-diffusion data of Wuensch et al. [1972], this work appears to support the case for non-structured Arrhenius plots. (At high concentrations of aliovalent diffusant, one would not expect to see any structure because D is independent of the grown-in vacancy concentration with $\beta \rightarrow 1$.) It is evident that further investigations would be useful to unravel the several interacting factors influencing the diffusion coefficient under these conditions.

6.6. High-diffusivity paths in MgO

There are apparently two mechanisms of short-circuit diffusion in single crystal magnesium oxide [Harding, 1971]. Both strontium [Mortlock and Price, 1972] and barium [Harding, 1967a] show enhanced diffusion over a wide temperature range which is independent of impurity precipitation. On the other hand, it has been found that Ni^{2+} diffusion is enhanced only below 1300 °C when impurity aggregates are known to be present at dislocations and grain boundaries [Wuensch and Vasilos, 1966; Mimkes and Wuttig, 1971]. This is supported by the small diffusion enhancements observed in this work for Mg^{2+} and Ni^{2+} at low temperatures. Oxygen grain boundary diffusion is also increased in the presence of iron [McKenzie et al., 1971].

From the diffusion standpoint, it appears possible to divide structural damage in MgO into three categories. The small degree of enhancement found for Ni^{2+} diffusion in MgO, for example, and the absence of any long tail in the concentration profiles, suggests that the mechanism responsible is probably not what is usually described as 'pipe' diffusion. Since the presence of impurity aggregates appears necessary for this type of diffusion to occur, there may exist a charge compensation effect that results in a 'halo' of vacancies around

the dislocation. This extra vacancy concentration over the equilibrium concentration for the lattice away from the dislocation could account for the larger diffusion coefficient seen in this region. Because of its extremely low solubility and large size, Ba^{2+} itself may well form immobile aggregates at these dislocations and hence show no observable diffusion enhancement by this mechanism.

For barium, diffusion enhancement appears to be caused by two types of defect, one giving rise to part B of the concentration profile which can be annealed out, the other more permanent and resulting in the long tails (part C) of the profiles. It is suggested that both these defects must be loose enough to enable the large Ba^{2+} ion to diffuse along them. Because of its high solubility and its size (close to Mg^{2+}) Ni^{2+} has no tendency to precipitate and diffusion enhancement along these defects does not occur in this case, except insofar as they would contribute to the 'halo' mechanism below, say, 1300 °C.

It is possible that the defects responsible for part B of the profiles are 'Stroh' cracks [Stokes, Johnston and Li, 1958, 1959] formed by the coalescence of edge dislocations. Lying in the (110) planes, they would provide a path component in the diffusion direction [100]. The long tails (part C) could arise from slits or microcracks in the [100] directions formed by the spreading of Stroh cracks along the length of edge dislocations. It would be interesting to perform further experiments to measure the degree of enhancement in different crystal directions in order to test these suggestions.

It is evident then, as concluded in section 5.3, that to obtain meaningful quantitative data for short-circuit diffusion in MgO , experiments must be done under carefully controlled conditions.

7. Conclusion

The diffusion in MgO single crystals of various cations, including Mg^{2+} , has been studied over a wide temperature range (up to 2500 °C) using radioactive tracers and a refined sectioning technique. The nature of high-diffusivity paths in MgO has also been discussed. The following conclusions can be drawn from the data obtained:-

(a) The dominant intrinsic defects in single crystal MgO are Schottky vacancies, the enthalpy and entropy of formation being (3.8 ± 0.3) eV and 1.8 k respectively.

(b) The enthalpy and entropy of motion of a cation vacancy are (1.56 ± 0.08) eV and 1.2 k respectively.

(c) There is no detectable dependence of the intrinsic activation energies for the diffusion of impurity ions in MgO (and hence of their enthalpies of motion) on ionic radius. MgO is, perhaps, similar to the alkali halides in this respect.

(d) Pre-exponential factors (D_0) for both intrinsic and extrinsic diffusion appear to depend mainly on mass for small ions, but increase linearly with polarisability for larger ions. It is this factor which gives rise to the observed 'size effect' on measured diffusion coefficients.

(e) Beryllium is likely to diffuse as an interstitial ion, but a small variation in activation energy for temperatures over 1900 °C suggests an increasing contribution from a vacancy mechanism.

(f) Impurity precipitation may well play an important part in controlling diffusion below 1500 °C, the principal element concerned being iron.

(g) From the results for germanium ion diffusion in MgO and a consideration of other published data, the enthalpy of motion of a

diffusing ion has been shown to be strongly dependent on its electronic charge.

(h) Short-circuit enhancement of diffusion in MgO occurs by two or more mechanisms, one involving the presence of impurity precipitates at dislocations. Such enhancement can therefore mask the presence of impurity-precipitation-controlled lattice diffusion. Large enhancements are found only for large ions (Sr^{2+} and Ba^{2+}), a result similar to that found in the alkali halides.

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